MAN'S IMPACT ON THE PHOSPHORUS CYCLE IN FLORIDA

By

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Abstract of Dissertation Presented to the Graduate Council of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

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A quantitative understanding of the phosphorus cycle in Florida is essential for resource management and pollution control of activities that release and utilize phosphorus, affecting eutrophication and economic vitality. Systems models of phosphorus flux were developed here for the Peace River Estuary, for the state of Florida, and for processes which may have been important in the original deposition of phosphate rock.

Digital computer simulation of the phosphorus flux in the Peace River Estuary showed the relative importance of projected changes in mining and population. The entire Peace River is high in phosphorus (all forms) ranging from 0.3 mg/l in Southern Charlotte Harbor to 1.0 mg/l in the Peace River Mouth. Since the natural drainage to the river is high in total phosphorus, daily mining water discharges to the river have little effect on total phosphorus concentrations. The

periodic spills from slime ponds in the mining district are more serious as shown by simulation of slime releases. Total phosphorus concentrations increase drastically for several days (20 mg/l total P) and level off at an average of 1.8 mg/l in the river mouth. Simulations indicate that, because tidal turbulence reworks the settled slime, phosphorus concentrations may remain elevated for many years.

Analog computer simulations were made of a model of productivity in the Peace River Mouth to show the effect of additional nitrogen on net photosynthesis and eutrophication. The simulation suggested that high phosphorus levels keep nitrogen levels low (less than 0.1 mg/l), the latter limiting net productivity. When nitrogen inputs from sewage and urban runoff are increased to levels corresponding to a population of 3 to 5 times the present population, net productivity increases to levels generally considered eutrophic (2.0 g O_2/m^3/day).

The percent effect on the overall geochemical cycle of the present phosphorus flows in peninsular Florida was determined by evaluating an overall phosphorus budget model for Florida. Overall phosphorus flows total 64 g/m^2/year. Through mining, Florida is draining its phosphorus supply 125 times faster than it is replaced. The phosphorus mobilized through mining is three orders of magnitude higher than the phosphorus cycling through Florida's waterways. The ratio of phosphorus in estuarine sediment to estuarine water

is 1,000 to 1. Fifty percent of the total input of phosphorus to inland waters is due to man's activities; these include sewage effluent (6%), agricultural runoff (34%), urban runoff (3%), and mining effluent (7%). Sewage going directly into estuaries is 9% of the phosphorus input to estuarine water. If the rate of phosphorus influx to sediment in estuaries is indicative, sedimentation rates are 0.76 m/1,000 years in Florida's estuaries. If isostatic adjustment is keeping pace with erosion, then the present rate of land elevation is .07 m/1,000 years.

Present ionic concentrations of Ca^{++}, HCO_3^-, and $HPO_4^=$ in surface and groundwater runoff indicate that phosphorus is being concentrated in rock through dissolution and reprecipitation with calcium phosphate increasing at the expense of calcium carbonate. Analog computer simulation of a systems model of this process suggests that enrichment can occur in 20 million years. The degree of enrichment depends on the supply of new phosphorus to Florida through rain and oceanic exchange processes. If the calcium phosphate content of original rock is .5 to 1.0%, a formation with 10 to 20% calcium phosphate as in the Miocene Hawthorn formation may result. Nutrient upwelling along the continental slope coupled with transport to the estuaries by lateral eddy diffusion can supply an additional 400 mg P/m^2-year which, if deposited, would result in a sediment with a 4.3% calcium phosphate content. If this is later enriched by resolution, 40% calcium phosphate results.

Using a systems model of the main energy and money flows, the energy budget of Polk County, Florida, for the present condition and for the condition without the mining industry was calculated. The energy budget for the present condition was 316.0×10^{11} kilocal/year; that for the condition without the mining industry was 303.6×10^{11} kilocal/year. For the present, the metabolic losses from the denuded land can be absorbed by the system. At the current rate of stripping land, however, within five to ten years the total energies for the county without phosphate mining will be higher than with mining.

INTRODUCTION

Often limiting to key processes in nature, agriculture, and industry, phosphorus is a major part of the systems of man and nature. Phosphorus moves through the land, air, and sea with concentrations in some rock deposits as in the phosphate deposits of Florida. The natural cycles of phosphorus have been much changed by the activities of man in mining, applying fertilizer, and releasing wastes. Phosphorus is one of the major nutrient elements affecting eutrophication in lakes, rivers, and estuaries and a critical factor in the agricultural and industrial economics of Florida. Understanding the phosphorus cycle is required for any sensible plans for resource management and pollution control. Florida offers a unique opportunity to examine the phosphorus cycle since one can find here examples of the benefits and problems associated with man's use of phosphorus (e.g., mining, lakes, estuaries, agriculture, and urbanization). What are the effects of man's development on the state's original phosphorus cycle? What happens under intensive agriculture and population growth? At what level are the resources of phosphorus? What kind of geochemical process generates these deposits and what kind of time is required to develop them?

To gain perspective of man's interaction with the phosphorus cycle, systems models were developed of the phosphorus cycle for the state of Florida and for the Peace River phosphate district and estuary. The Peace River district is uniquely rich in phosphorus and is the projected site of the largest future population growth in Florida so that management for phosphorus wastes becomes an important part of the total ecological engineering concerns of this area. The systems model of phosphorus flux in peninsular Florida quantifies the rates of flow and present storages so that flows can be examined in terms of their percent effect on the overall geochemical cycle. The effect of population growth and alternatives of water and waste management are tested with calculations and simulations.

Explaining the origin of the phosphorus concentrations in sedimentary phosphate rock deposits and determining the rates of formation requires considerations over geologic time. A systems model of geochemical replacement is used to evaluate the pathways of dissolution and reprecipitation of calcium carbonate and calcium phosphate in the soil and rock.

Previous Studies on Phosphorus Cycles

The literature on phosphorus and phosphorus cycling is extensive. Surveyed here are theories on the origin of phosphate rock deposits, three landmark papers on

the biogeochemical cycling of phosphorus, and the history of theories on recycling phosphorus from the ocean.

Early Papers on Florida's Phosphate Rock Deposits

Sellards (1913) summarized the theories on the origin of Florida's mineable phosphate rock deposits. Several early writers (Ledoux, 1890; Cox, 1891; Darton, 1891; and Dall, 1892) suggested bird guano deposits as the source. They suggested that phosphoric acid leached out of the guano and replaced calcium carbonate with calcium phosphate. Dall suggested that the local character of the bird rookeries determined the local character of the phosphate rock. More recently, Vernon (1951) developed the guano theory, stating that limestone islands existed with bird rookeries on them during the Miocene and younger epochs. Rainfall dissolving the guano allowed phosphoric acid to penetrate the limestone and form a crust of calcium phosphate. He stated that "large colonies of birds on land may also increase the amount in solution in adjacent sea waters which then support a thriving population of phosphorus using organisms." The guano producing birds (large birds which feed over a wide area and return to restricted sites for rest) are pelicans, boobies, and cormorants. Birds began evolving during Cretaceous time and were well established in the geologic record by Miocene time. Hutchinson (1950) stated that large colonies of birds on a section of coastline, when the form of the substrate permits guano to be returned to the ocean, steepens

the nutrient gradient resulting in increased littoral productivity. A steady state was established in which a phosphorus rich ocean supplied food for the birds; excrement from the birds returned phosphorus to the sea and completed the cycle. A few guano forming birds have been found in the Miocene in Florida. They include several cormorants and a booby (Brodkorb, personal communication). However, the Bone Valley formation of Pliocene age contains abundant bird remains (Brodkorb, 1955). Brodkorb identified 135 specimens of the small cormorant Phalacrocorax wetmorei in the Bone Valley. He believed that the Bone Valley phosphates were concentrated from the Hawthorn phosphates through guano producing birds. Specifically, he stated that erosion of the Hawthorn formation produced a phosphate rich sea with high productivity. The excrement of cormorants and boobies, which feed on the top of the food chain in the ocean and group on land to rest, was then the means by which the Bone Valley phosphates formed.

Among the early writers, Davidson (1892), Brown (1904) and Sellards (1931) believed that percolating water was the mechanism responsible for concentrating phosphorus. Sellards stated, "the rainfall (high in Florida) in passing through the surface materials dissolves a limited amount of the phosphate which is carried to a lower level and precipitated in a concentrated form. This process long continued results in the accumulation of workable phosphate deposits." More

recently, Odum (1951), in noting that phosphorus concentrations are higher in acid surface water than in groundwater, used tables of solubility of phosphates and pH to suggest that phosphorus was dissolved by acid surface water but precipitated again as percolating water became basic.

"The Geologic Role of Phosphorus" by Eliot Blackwelder, 1916

Blackwelder may have presented the first complete discussion in the literature of phosphorus cycling. Although nonquantitative, insights into the overall phosphorus cycle and subordinate cycles were stated. Phosphorus in meteorites, in igneous rocks, in sediment and sedimentary rock, and in the ocean were discussed. Theories on phosphate deposition were examined as well as pathways from one storage location in the cycle to another. He stated that all igneous rocks contain phosphorus as apatite averaging 0.29% P_2O_5. The basic igneous rocks had the highest content (0.5 to 1.15% P_2O_5). High grade phosphate rock could occur in pegmatites as exemplified by the nelsonite of Virginia. Primary phosphorus found in igneous rocks was dissolved by percolating water, providing nutrients for plants and animals and ultimately the source of phosphorus for sedimentary rocks. Blackwelder further pointed out that the phosphorus in the ocean seems to have reached the most dilute state in its cycle. Its only escape from the sea, he said, is through birds and fishing. In discussing the origin of

phosphate nodules in the sea and phosphate rock of marine origin, he stated that phosphorus sedimentation could only occur where the quantities of decomposing matter were too great for scavengers to completely decompose. An anaerobic environment, he contended, was a controlling chemical condition implying that areas of restricted circulation in the ocean were the sites for phosphate deposition with collophane being the original phosphate compound formed. The amorphous collophane was gradually converted to apatite. He briefly presented the idea that phosphate may be enriched in limestone due to percolating waters when he said, ". . . the lime carbonate is relatively more soluble than the lime phosphate. Therefore, during the slow process of solution by rainwater descending from the surface, the calcium phosphate, although actually decreased in total quantity, has been relatively concentrated by differential solution."

"The Biogeochemistry of Phosphorus" by G. Evelyn Hutchinson, 1952

Hutchinson presented the first real quantitative examination of the phosphorus cycle. He discussed the cosmic background of phosphorus, its natural history and its movement in the biosphere. Summaries of the structure of apatites, occurrence of phosphate in primary rocks, in the pedosphere, in the atmosphere (phosphine gas), in the hydrosphere, and in guano deposits were presented. Salient points with respect to the structure of apatites included

the fact that the hydroxyl ions in apatites of biological origin are exchanged for fluoride ions in dilute aqueous solution. Furthermore, it appeared that when apatite skeletons came in contact with sea water a considerable amount of fluorine was incorporated into the lattice structure.

After reviewing the extensive literature on phosphorus in primary rock, Hutchinson concluded that the best estimate for the mean value is .12% P. Phosphorus content declines with increasing silica in igneous rock; basalt contains .2% and rhyolite .02%. Sediment, he contended, is intermediate between basalt and rhyolite with continental regions underlain by granite having less than their share of phosphorus.

Since phosphates are slightly soluble in water, a small amount of phosphate occurs in soil solution. After entering plants, it has a long metabolic industry and is eventually returned to the soil except where crops are removed to be eaten elsewhere. The important consideration as far as soil phosphates are concerned is fixation of soluble forms as calcium, aluminum, or iron phosphates resulting in a lowered availability of phosphorus to plants.

In the hydrosphere, phosphorus in inland waterways and in the oceans is of prime importance to primary productivity. Hutchinson obtained an average river concentration for the world of 0.1 mg/l total phosphorus. The importance of the exchange of phosphorus between mud and water was discussed in noting the extraordinary dilution at which phosphorus can

be used. In the ocean, there was a continual drain on phosphorus in the photic zone due to the sedimentation of planktonic organisms. Hutchinson gave the overall average phosphorus concentration of the ocean as 0.093 mg/l total P. Pointing out that this is the same order of magnitude as influent river water, he concluded that the replacement of phosphorus in the ocean must occur almost as frequently as that of water (once every five million years). A maximum residence time for phosphorus of twenty million years was calculated, indicating that the phosphorus in the ocean had been lost and restored many times. The return of phosphorus to the land occurs slowly being mediated only by birds, man, and geologic uplift.

Hutchinson was the world's pioneer in showing the role of guano in the phosphorus cycle (see Hutchinson, 1950). He pointed out in this overview paper that divergence of surface waters in the latitudes of the trade winds along the west coasts of continents caused upwelling of nutrient rich deep ocean water. The result was fertile ocean waters with high primary productivity forming the base of a food chain which ends with birds. The birds then deposit the phosphate from the deep ocean in the form of guano deposits which, on desert islands such as the Peruvian guano islands, simply accumulates. On islands with occasional rain, the soluble components of the guano are leached out, leaving the calcium phosphates.

"The Acceleration of the Hydrogeochemical Cycling of Phosphorus" by Werner Stumm, 1972

Recently, at the Nobel Symposium in Sweden, Stumm presented a landmark paper on phosphorus in which he addressed the question of man's role in phosphorus cycling rates and storages. Stumm presented a global phosphorus circulation model which included the abundance in terrestrial and marine plants, in soils, sediment, and water, and in the earth's crust. Transfer rates between compartments were given. From examination of rates, he concluded that man, through mining, is restoring incipiently marine phosphorus to the land at higher rates than it washes to the sea. The result is "ecological imbalance causing pronounced pollution in inland and coastal waters." Noting that the annual uptake of phosphorus by phytoplankton in the sea is much higher than the annual contribution of phosphorus to the oceans, he concluded that most of the phosphorus flowing through the phytoplankton is continuously regenerated from organic debris. Stumm pointed out from the photosynthetic equation that for every phosphorus atom respired, 276 oxygen atoms have been consumed. Thus, any increase in the supply of phosphorus to the sea, even if it has a negligible effect on the overall phosphorus content of the ocean, will increase the fraction of ocean floor which is anaerobic.

In discussing pollution of inland waters, Stumm stated that the organic material introduced to a lake from sewage may be quite small in comparison to the organic material

synthesized from the phosphorus in the water. If phosphorus is limiting, 1 mg of phosphorus allows the synthesis of about 100 mg of algal biomass. When this biomass settles it exerts a biochemical oxygen demand of about 140 mg. Estuaries are apparently an area of great concern because they are efficient in trapping nutrients.

In discussing the formation of marine phosphorites, Stumm proposed three mechanisms: (1) burying of detrital phosphorus, (2) chemical precipitation of apatite, and (3) diagenetic replacement of calcite by substitution of carbonate by phosphate. He believed that apatite precipitation on the seafloor is unlikely unless the relative degree of apatite saturation has increased and favorable conditions for nucleation prevail. Unless the system is anaerobic, regenerating detrital phosphorus does not increase the degree of saturation because the regeneration also liberates CO_2 which increases the acidity. For the degree of saturation to increase, this CO_2 must somehow be lost from the system. Stumm believed that areas of upwelling are likely sites for apatite precipitation since the CO_2 is lost to the atmosphere in this system. In other words, increasing phosphorus concentrations may not precipitate apatite, but increasing the pH of the water may initiate it.

In investigating the kinetics of apatite formation. Stumm found that three steps are involved: (1) sorption of phosphate forming amorphous calcium phosphate, (2) transformation of the amorphous nuclei into crystalline apatite,

and (3) crystal growth of apatite. He also found that calcite will convert into apatite in sediments although the change is quite slow.

Finally, Stumm concluded that mining production, which increases the flux of phosphorus to inland waters, to estuaries, and to the ocean, is creating undesirable conditions in lakes and estuaries and causing oxygen deficits in parts of the ocean. As first steps in controlling this, he suggested a re-examination of the present practice of excessively fertilizing land and improvement of the presently inefficient waste treatment systems.

Studies on Phosphorus Recycling from the Ocean

The ultimate recycle pathway and an important one in the considerations here is the means by which phosphorus moves from the ocean to the land. Mediation by pelagic birds has been discussed previously; however, several other pathways may also be important.

Conway (1943), as cited in Chesselet et al. (1972), considered a "cyclic salts" hypothesis. He showed that part of the salts dissolved in rivers had a marine origin. A steady state salinity for the oceans requires that some fraction of the salt must be recycled onto land. Barth (1952) and Goldberg (1963) later demonstrated that these salts must be injected into the atmosphere at the surface of the oceans and fall out with rain onto the continents.

Sugawara (1961) demonstrated that the constant proportion of ions in sea water is not found in the atmosphere; therefore, an evaluation of the fraction of salts recycled is difficult and remains obscure to date. Woodcock (1953) showed that the mechanism of particle injection into the atmosphere depends on the action of the wind on the sea. When wind conditions over the ocean are such that whitecaps appear, waves and surf splash sea water into the atmosphere, forming ion-containing aerosols. Probably more important, however, is the continuous formation of marine aerosols by bubble collapse at the sea's surface over all the ocean (Blanchard, 1963). Baylor et al. (1962) and Sutcliffe et al. (1963) showed that bubbles rising through sea water adsorb phosphates and that phosphate is ejected from the surface of the ocean by the bursting of wind and wave induced bubbles. The bursting bubbles were found to contain a greater concentration of phosphate than the sea water (1.41:1 for PO_4 in the aerosol to PO_4 in the sea water). Some fraction of phosphorus in rain, then, originates in the ocean and is recycled onto the land.

In geologic time, phosphorus may be recycled from the ocean through estuarine sediment which becomes land as sea level changes. Phosphorus concentrations in the ocean are quite small (often less than 0.01 mg/l at the surface) unless special conditions exist. It is a well-established fact that upwelling of nutrients occurs in locations where prevailing

strong winds parallel to or off the land push water off the coast, allowing it to be replaced with deep nutrient-rich water. The best known example is along the coast of Peru where nutrient-rich surface waters support large phytoplankton populations. The first suggestion of upwelling as a source of phosphorus for phosphate rock is in a paper by Kazakov (1937) where he states that upwelling of deep phosphate-rich ocean waters along steeply inclined continental slopes brings phosphates onto the relatively shallow areas of the continental shelf. This "extra" phosphorus may be taken up in the food chains and eventually be deposited in the sediment, or it may precipitate directly. Dietz et al. (1942), in making calculations on the theoretical amount of phosphate ions that can exist in sea water, found that the sea is several hundred percent saturated with phosphate. Although there are many sources of error in this calculation, such as the effect on the solubility of calcium phosphate of temperature, pressure, and the presence of other ions, Dietz et al. believe that sea water, at least in its deeper colder portions, is essentially saturated with calcium phosphate. Furthermore, they postulate that slight changes in the physical-chemical or biological conditions in the sea may bring about supersaturation. It is known that dissolved phosphorus is high in the cold waters of deep ocean basins (Sverdrup et al., 1942). Upwelling of deep water to shallow, agitated, and warmer zones may cause a loss of dissolved

CO_2, an increase in pH and supersaturation of phosphate.

The phosphate nodules occurring off the coast of southern California are often cited as examples of phosphate forming at the present time. Similar nodules occur in other oceanic areas (western coast of South America, western and southern coasts of Africa, and south of New Zealand). Kolodny and Kaplan (1970), using radioactive age dating of the U^{234}/U^{238} isotopes, which are associated with the phosphorite, found all the nodules to have a minimum age of 800,000 years; indications were that they are probably older than that. No recently forming apatite was detected in their study. The phosphorite nodules found in today's oceans occur along the continental slope edge; they are generally not found in shallow shelf areas.

Assuming phosphorus of oceanic origin is deposited in shallow water sediment, this phosphorus may become part of a continent through sea level lowering and uplift of the land. The geologic record indicates that sea level fluctuations have occurred throughout geologic time. The details of large fluctuations during the recent pleistocene epoch are recorded in coastal rock. What is now Florida has been below sea level and large expanses of the Florida shelf have been above sea level many times (Cooke, 1945). During low sea level stages when the water was in glaciers, exposed continental shelf areas may rebound isostatically due to the unloading of water. Studies on Lake Bonneville in western

Utah seem to verify this (Crittenden, 1963). An average load of 145 m of water covered an area of about 50,000 km^2 there. Since removal of the water some 15 to 25 thousand years ago, once level shorelines have undergone a broad domical uplift of about 64 m (210 feet) in the center. The indication is that uplift may coincide with sea level lowering.

Phosphorus Systems in Florida

Several systems in Florida were selected and defined for modeling, calculations, and simulation. Some background and introduction to these follows next.

The Peace River - Charlotte Harbor Estuarine System

Charlotte Harbor (Figs. 1 and 2),located on the Gulf coast of Florida approximately 60 miles south of Tampa, is one of the largest and least contaminated (Alberts et al., 1970) estuarine complexes in Florida. The system is a drowned estuary enclosed by a series of barrier islands, the most famous of which is Sanibel Island located at the southern end. Tidal exchange is controlled by two major inlets -- Boca Grande Pass on the West and San Carlos Bay on the south end. Three rivers drain into the harbor -- the Peace, the Myakka, and the Caloosahatchee. The total harbor, including islands, occupies an area of 280 square miles with a total shoreline of about 40 nautical miles (Huang and Goodell, 1967).

Figure 1. Map of Florida showing the area included in the peninsular Florida model, the drainage of the phosphate mining district, and the edge of the Florida Plateau. The northwestern boundary of the peninsular Florida model is the Suwannee River; total area is 10^{11} m^2.

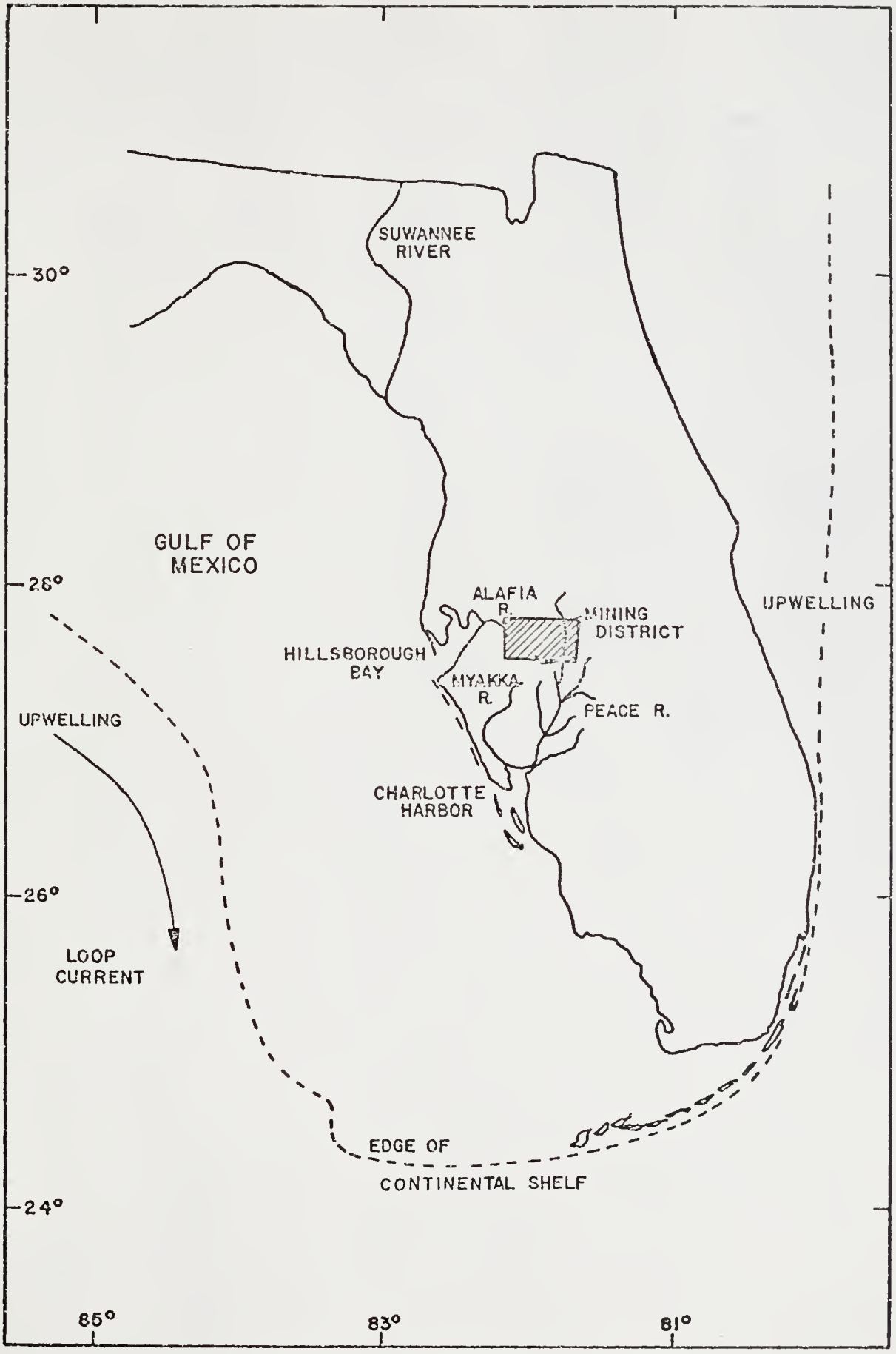
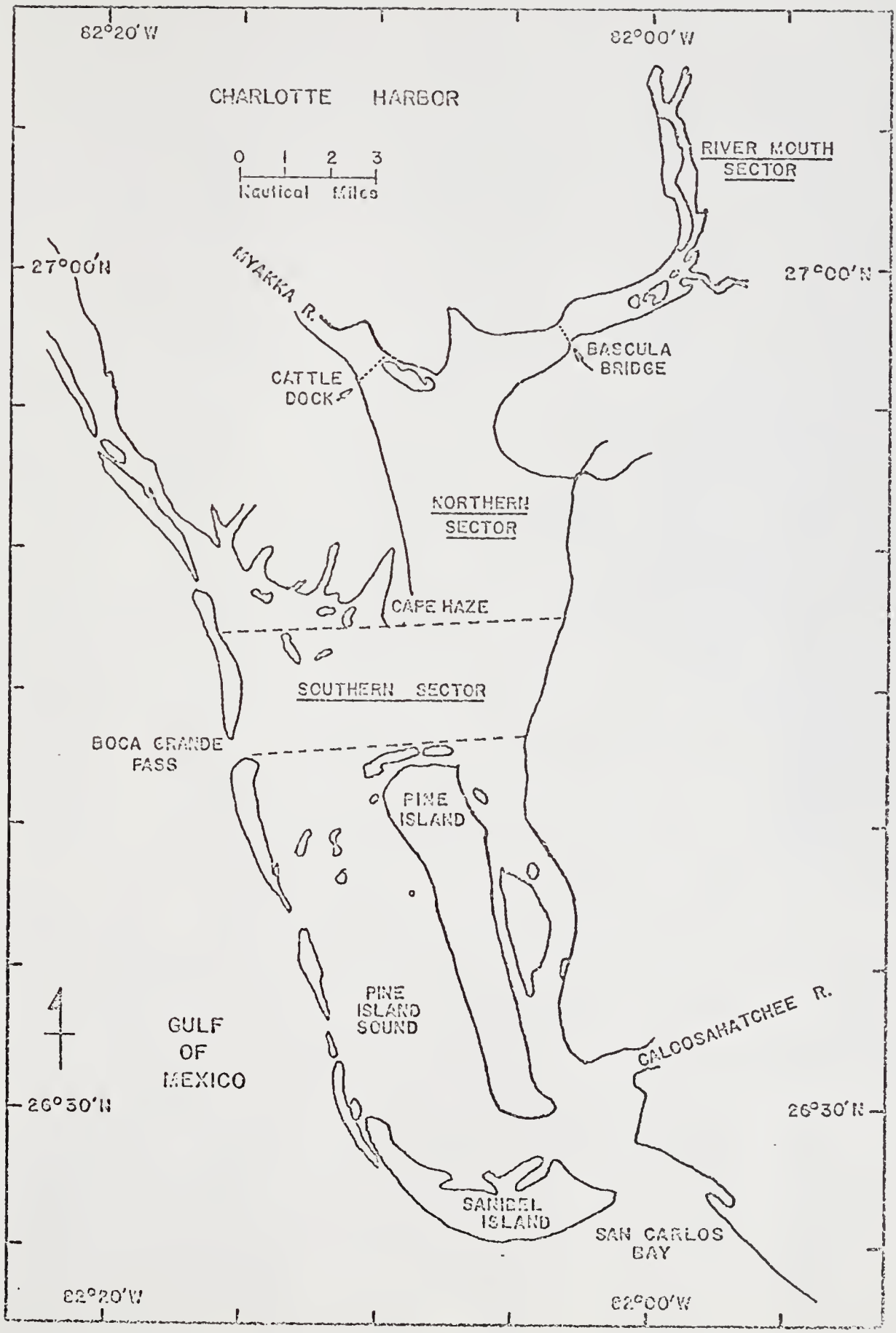

SUWANNEE RIVER
30°
GULF OF MEXICO
28°
ALAFIA R.
MINING DISTRICT
HILLSBOROUGH BAY
MYAKKA R.
PEACE R.
UPWELLING
UPWELLING
CHARLOTTE HARBOR
26°
LOOP CURRENT
EDGE OF CONTINENTAL SHELF
24°
85°
83°
81°

Figure 2. Peace River - Charlotte Harbor Estuarine System showing the physical location of the storages defined in the model (Figs. 9 and 10).


82°20'W
82°00'W
CHARLOTTE HARBOR
0 1 2 3
Nautical Miles
RIVER MOUTH SECTOR
27°00'N
MYAKKA R.
27°00'N
BASCULA BRIDGE
CATTLE DOCK
NORTHERN SECTOR
CAPE HAZE
SOUTHERN SECTOR
BOCA GRANDE PASS
PINE ISLAND
PINE ISLAND SOUND
GULF OF MEXICO
CALOOSAHATCHEE R.
26°30'N
26°30'N
SANIBEL ISLAND
SAN CARLOS BAY
82°20'W
82°00'W

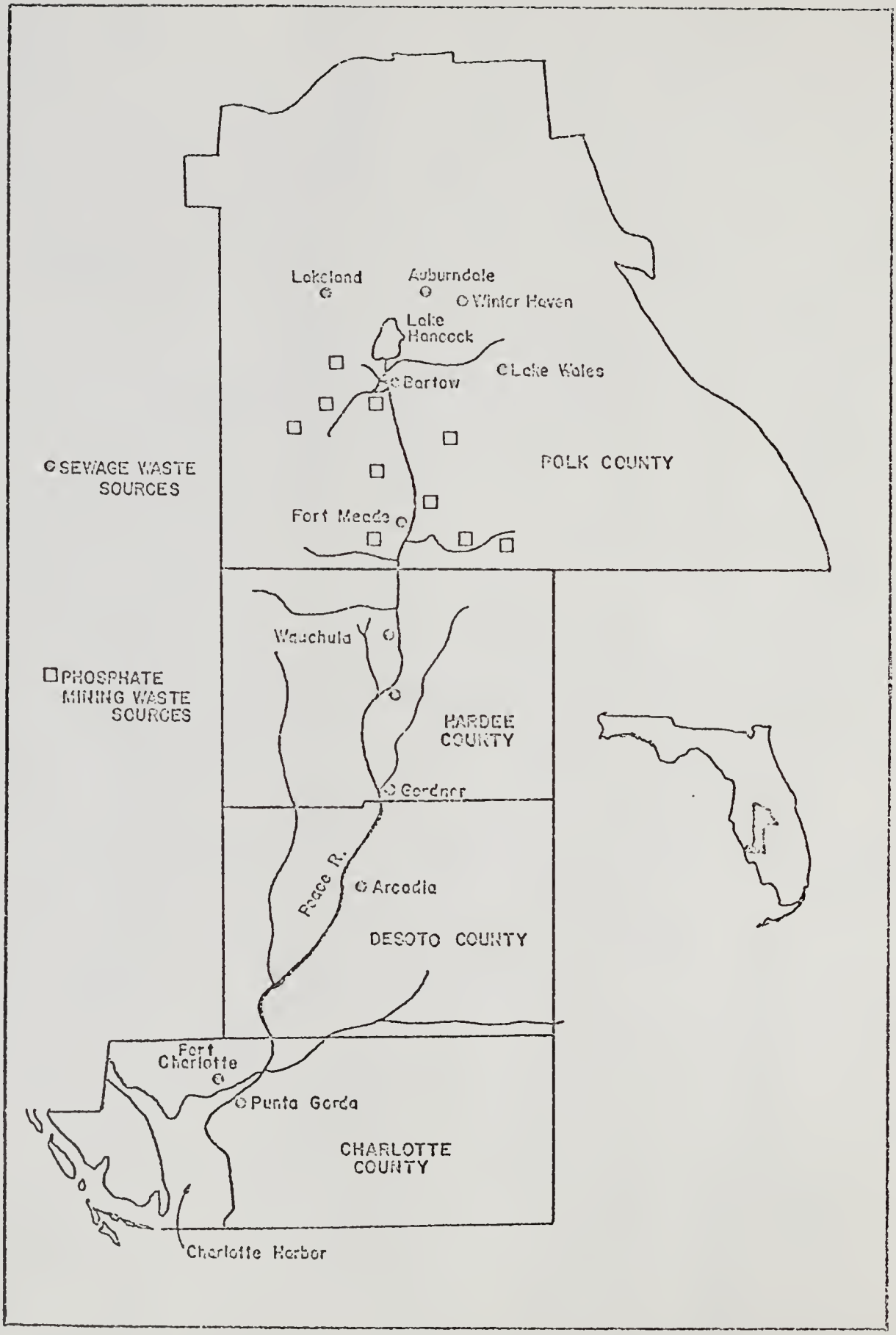
The Peace River begins at Lake Hancock, forming one mile east of Bartow by the juncture of Peace Creek and Saddle Creek Canal (Fig. 3). It extends 98 miles southward, emptying into Charlotte Harbor at the town of Punta Gorda. Average depth of the river is three to eight feet with a maximum depth at Arcadia of twenty feet (Lanquist, 1953). The width of the river varies from 60 to 200 feet.

Phosphorus enrichment of the Peace River - Charlotte Harbor estuarine complex is a result of the natural rich geochemical cycle of phosphorus in the area and a result of the urban expansion of man. Questions of regulation of waste discharge in the Peace River Basin require understanding of the present state of phosphorus and factors affecting its flows.

Natural Areas

The surface geology of the land area consists of post-Eocene rocks which are primarily limestone and dolomite with sand, clay, and phosphate (Cooke, 1945). Karst topography is evident, resulting from heavy rainfall on the calcaceous rock. The Peace River basin consists of rolling sandy hills, swamps (some of which have been made into canals), and many small lakes (some of which have been connected to surface water drainage and some of which drain through the ground). These many small lakes exert a buffer effect on streamflow. Streamflow does not fluctuate rapidly since the lakes store water in times of excess rainfall, reducing the flood peaks.

Figure 3. Peace River from its source north of Bartow to its mouth at Charlotte Harbor. Sources of phosphate wastes to the river are shown.


Lakeland
Auburndale
Winter Haven
Lake Hancock
Lake Wales
Bartow
SEWAGE WASTE SOURCES
POLK COUNTY
Fort Meade
Wauchula
PHOSPHATE MINING WASTE SOURCES
HARDEE COUNTY
Gardner
Peace R.
Arcadia
DESOTO COUNTY
Fort Charlotte
Punta Gorda
CHARLOTTE COUNTY
Charlotte Harbor

Along the Peace River proper, upland pine and oak forest predominate, surrounded by pine flatwoods (slash and longleaf pine). Mangroves occur along the east coast of Charlotte Harbor. At the mouth of the Peace River is a swamp forest consisting of water oak, laurel oak, sweet gum, and cypress. Intermittent cypress swamp can be found from Bartow to Fort Meade.

Lanquist (1953) in a biological survey of the Peace River attempted to correlate the chemical and physical factors with the fauna. He found that the substrate in the river was usually sand, phosphatic slime, or hyacinth detritus and is of great importance in determining the nature of the community. Deposition of phosphatic slime from spills destroyed animal habitats and vegetation. J. Dequine in personal communication indicated there may be direct effects on gill actions of fish.

In a study of the small estuarine fish of Charlotte Harbor, Wang and Raney (1971) found an abundance and diversity of juveniles and euryhaline fish near the mouths of the Peace and Myakka Rivers. Dominant fish are the bay anchovy (Anchova mitchilli), the pinfish (Lagodon rhomboides), the silver perch (Bairdiella chrysura), the silver jenny (Eucinostomus gula), and the seatrout (Cynoscion arenarius).

The geochemistry and hydrography of Charlotte Harbor have been examined by Alberts et al. (1970). They sampled the system for salinity, temperature, and dissolved

phosphorus in surface waters, bottom water, and interstitial water. Water temperature in August averaged 30°C, in December 16°C and in March 19°C. The salinity structure was one of decreasing salinity from Boca Grande Pass to Punta Gorda at the Peace River Mouth (Fig. 2). Just inside Boca Grande Pass at high tide the salinity was 30 °/oo; at low tide 15 °/11. At Punta Gorda at high tide the salinity was 12 °/oo; at low tide 1 °/oo.

Human Settlements

Man's technological systems affect the great diversity in ecosystem types in the Peace River area. These include agriculture, urban areas, and especially the phosphate mining district in Polk County. Table 1 has statistics related to agriculture and urbanization for the four counties through which the Peace River flows. The large, growing population of Charlotte County is significant since it surrounds the estuarine portion of the Peace River. Sewage from 200,000 people is presently discharged into the Peace River. Manufacturing in the area includes principally food processing and chemicals employing 17,300 people in Polk County and 780 in the other three counties. The fishing industry in Charlotte Harbor grosses 3,444,000 pounds of fish per year which sells for $646,000.

Most of the farm land (Table 1) is pastureland which receives little subsidy in terms of fertilizers. The area is a major citrus producer with about one-fourth of Florida's production coming from Polk County (Fla. Stat. Abst., 1971).

Table 1

Statistics[a] for Counties Through Which the Peace River Traverses

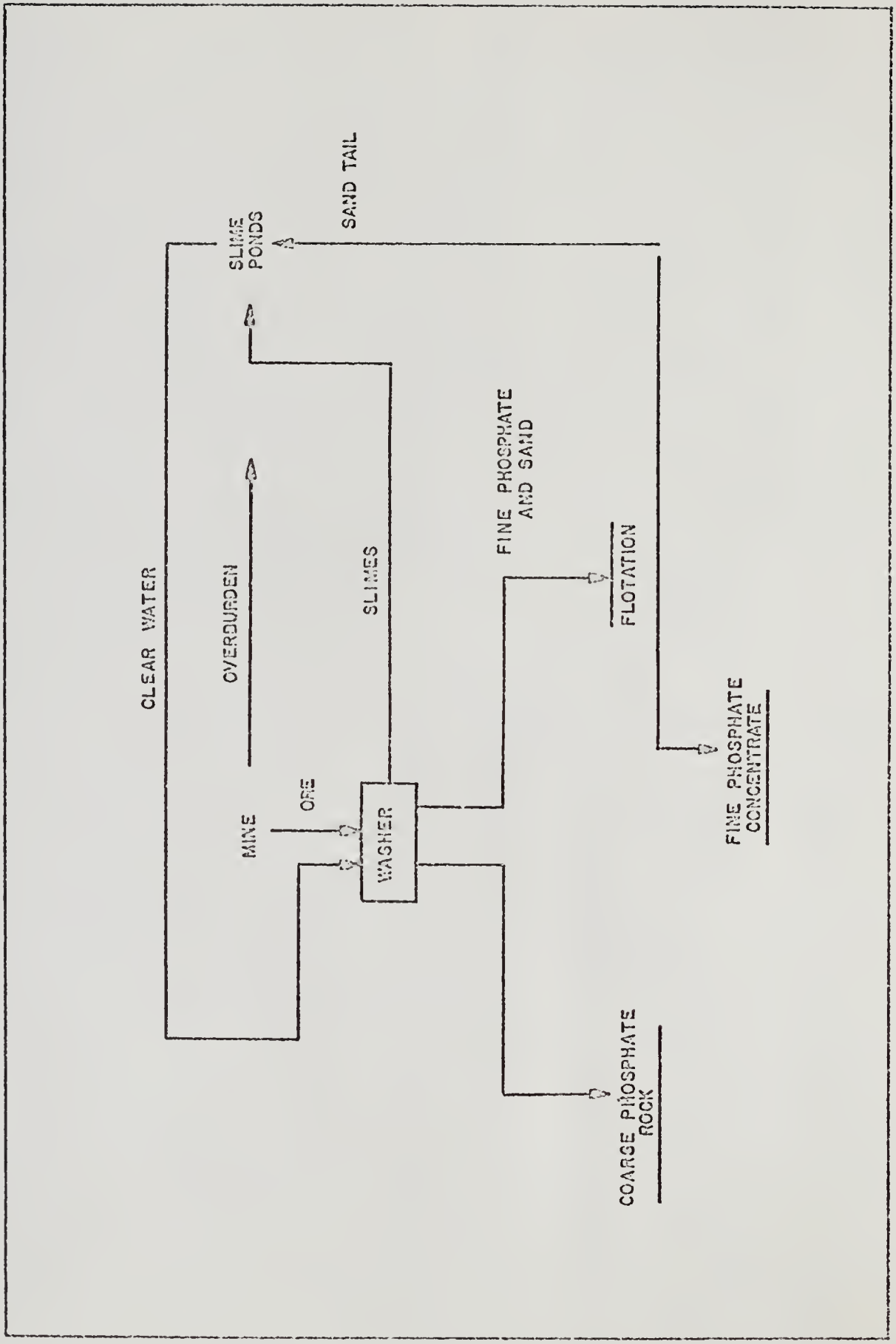
County	Population (1970)	Increase in population from 1960-1970 (%)	Population living in urban areas (%)	Total area (mi^2)	Land as farms (%)	Value of farm products sold ($1,000)
Polk	227,222	16.4	61	2,048	90	130,779
Hardee	14,889	20.4	20	630	97	18,907
DeSoto	13,060	11.8	43	651	71	6,525
Charlotte	27,559	118.8	60	832	60	1,425

[a]From Fla. Stat. Abst., 1971.

Vegetables grown include cabbage, cauliflower, tomatoes, beans, cucumbers, squash, and strawberries. Few field crops are grown. Total dollar value of the farm products sold in the four counties is $157,646,000 (Table 1).

The phosphate mining industry in Polk County exerts the greatest influence on the entire Peace River - Charlotte Harbor system. Commercial grade phosphate rock occurs as pebble size nodules (>1 mm) to a fine clay in the lower half of the Bone Valley formation. Pebble phosphate is in a deposit five to forty feet thick and ten to sixty feet below the surface (Boyle, 1969). The matrix, a term used to mean the ore or that part that can be economically mined, is 30 to 60% phosphate rock, 10 to 25% quartz sand, and 15 to 40% clay and colloidal phosphate. Obtaining the high grade rock involves strip mining where draglines with bucket sizes up to 40 cubic yards remove the overburden and deposit it in spoil banks along the side of the cut. Nine cubic yards of overburden must be removed to obtain thirteen cubic yards of matrix (Boyle, 1969). The phosphate rich material is slurried into a pit by hydraulic guns which use 10,000 gallons of water per minute. This slurry of phosphate, quartz sand and clay is pumped through fourteen-inch pipes to the washer plant where the sand and clay are removed by washing, screening, and flotation (Fig. 4). The waste water is routed to hydroseparators which separate clear water from slime. The clear water is recycled and the slime is routed to settling ponds. Total water usage of the industry is

Figure 4. Flowsheet of a Florida phosphate rock mining and beneficiation plant (from Env. Prot. Agency, 1971a).


SAND TAIL
SLIME PONDS
CLEAR WATER
OVERBURDEN
SLIMES
FINE PHOSPHATE AND SAND
FLOTATION
MINE
ORE
WASHER
FINE PHOSPHATE CONCENTRATE
COARSE PHOSPHATE ROCK

77,200 gallons per minute with 22,000 gallons (26%) coming from deep wells and 57,200 gallons (74%) reclaimed from processing and settling ponds (Boyle, 1969). The slimes are nine to twenty-six percent solids by weight (Specht, 1950) and would take as long as 30 years to settle (Specht, 1950). Since the major constituents of the wastes are clay minerals whose retention of water increases their volume six to ten times, the volume of wastes exceeds the original volume of rock removed by 1.25 times to 1.5 times. As a result, the waste will not fit entirely in the mined-out pits and diking above grade is required. This is hazardous due to potential spillage and, in fact, dozens of slime spills have occurred in the past 25 years (Dequine, personal communication). Major slime spills, due to the toxicity and high turbidity, kill river fish and cause heavy mortality of the benthic invertebrates.

Other problems in the industry include air pollution (particulate dust, sulfur dioxide, and fluoride emissions) from beneficiation of the ore. Wastewater with high phosphorus, nitrogen, and fluorine contents at one time was discharged to the rivers. However, presently it is partially recycled.

In summary, the mining industry in Polk County has transformed about 50,000 acres of farms, forests, and pastures into spoil banks, slime impoundments, and water-filled pits. Natural plant succession has produced young forests in some areas.

Peninsular Florida

Since benefits and problems associated with man's use of phosphorus are exemplified in Florida, it offers a unique opportunity for examining phosphorus cycling and man in a quantitative manner. Florida produces three-fourths of the nation's marketable phosphate rock and one-third of the world's (Florida Phosphate Council, 1973); a sophisticated agricultural system, with its associated superphosphate fertilizer use, exists in the state; Florida's many lakes are subject to nutrient enrichment; its highly urbanized areas have the usual associated nutrient waste disposal problems; and its many estuaries acting as the final nutrient trap are subject to enrichment and associated depleted oxygen supplies.

The Environmental Protection Agency as well as Florida's State Pollution Control Board is currently attempting to fix wastewater effluent standards for phosphorus. For example, the Wilson-Grizzle Bill passed in the Florida State Legislative session of 1972 requires the city of Tampa to use advanced waste treatment processes for phosphorus removal to 1 mg/l P. Tampa sewage is discharged into Hillsborough Bay which experiences the algal blooms and anaerobic bottom waters associated with nutrient enrichment.

Criteria presently used to determine effluent standards are often qualitative or refer to concentrations. For setting standards for effluent, limits stated as

concentrations may be less useful than limits on percent effects on existing flows. Few quantitative data on flows have been prepared for regional or statewide systems. Demonstration of this new approach is done here in evaluating phosphorus cycling in the state; the percent effect of each flux on the overall chemical cycle is determined. State water quality programs based on this sort of quantitative data may be more meaningful and efficient.

As higher standards for phosphorus in domestic wastewater and mining wastewater effluent are met, Florida's population continues to grow exponentially so that the net gain in water quality may be negligible. In order to evaluate this, a clear quantitative understanding of phosphorus storages and rates of flow from storage to storage must be acquired.

The evaluation of phosphorus cycling in peninsular Florida (Fig. 1) done here examines the magnitude of the outside sources of phosphorus to the state, of the storages and recycling pathways within the state, and of the phosphorus losses from the state.

Florida's Phosphate Rock Deposits

In order to understand and calculate rates of formation of Florida's phosphate rock, data on the geologic formations and their phosphorus contents are pertinent. For reference a Cenozoic time scale with the principal Florida formations is included as Table 2.

Table 2

Cenozoic Time Scale

Period	Epoch	Name of main formation* of this age in Central Florida	Time in millions of years	Cumulative time from present in millions of years
Quaternary	Recent			
	Pleistocene		1	1
Tertiary	Pliocene	Bone Valley formation, Alachua formation	10	11
	Miocene	Hawthorn formation Tampa limestone	14	25
	Oligocene	Suwannee limestone	15	40
	Eocene	Ocala limestone	20	60
	Paleocene	Cedar Keys limestone	10	70

*There is a controversy regarding the exact age and extent of the Hawthorn and Bone Valley formations; this table shows the distribution given by Altschuler et al. (1964).

Florida stratigraphy is dominated by a thick series of shallow marine deposits, principally limestone, ranging in age from Lower Cretaceous to Recent. The principal structural feature is the Ocala Uplift, a broad oval arch trending N-NW and centering in Levy or Marion County (Cooke, 1945). The Ocala limestone of Eocene age is exposed at the surface on the Ocala arch. This limestone is the dominant stratigraphic unit underlying most of Florida; solutional features in the Ocala limestone cause the Karst topography typical of much of northern peninsular Florida. Although Oligocene rocks are absent in much of Florida, the Suwannee limestone of late Oligocene age occurs in West Central Florida in the region of the land pebble phosphate district. Both the Ocala and Suwannee limestones are quite pure, being 91 to 98% $CaCO_3$. The Tampa limestone of early Miocene age lies on the eroded surface of the Suwannee limestone (Cooke, 1945) in the northern part of the phosphate district. It is an impure sandy and clayey limestone containing chert nodules and trace amounts of phosphate (Altschuler et al., 1964). For reference, the location of the land pebble phosphate district and a stratigraphic cross-section through it are shown in Figs. 5 and 6, respectively.

Of particular interest in this study is the Hawthorn Formation of middle Miocene age. It consists chiefly of gray phosphatic sand and lenses of green or gray clay (Cooke, 1945). It is thought to consist of the deposit of

Figure 5. Map of west-central peninsular Florida showing the limit of the land-pebble phosphate district (dashed line). Section A-A' is shown in Fig. 6 (taken from Altschuler et al., 1964).

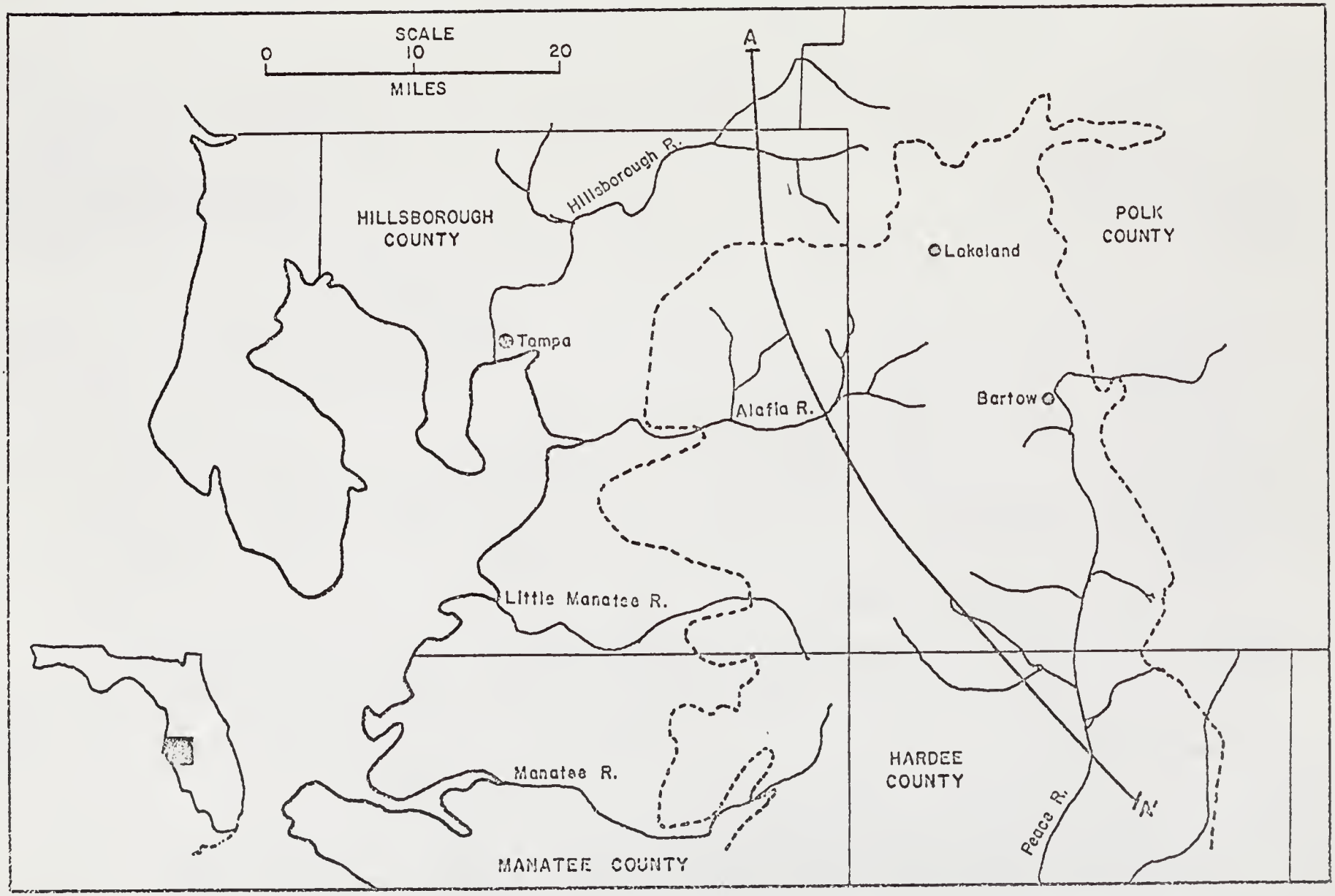
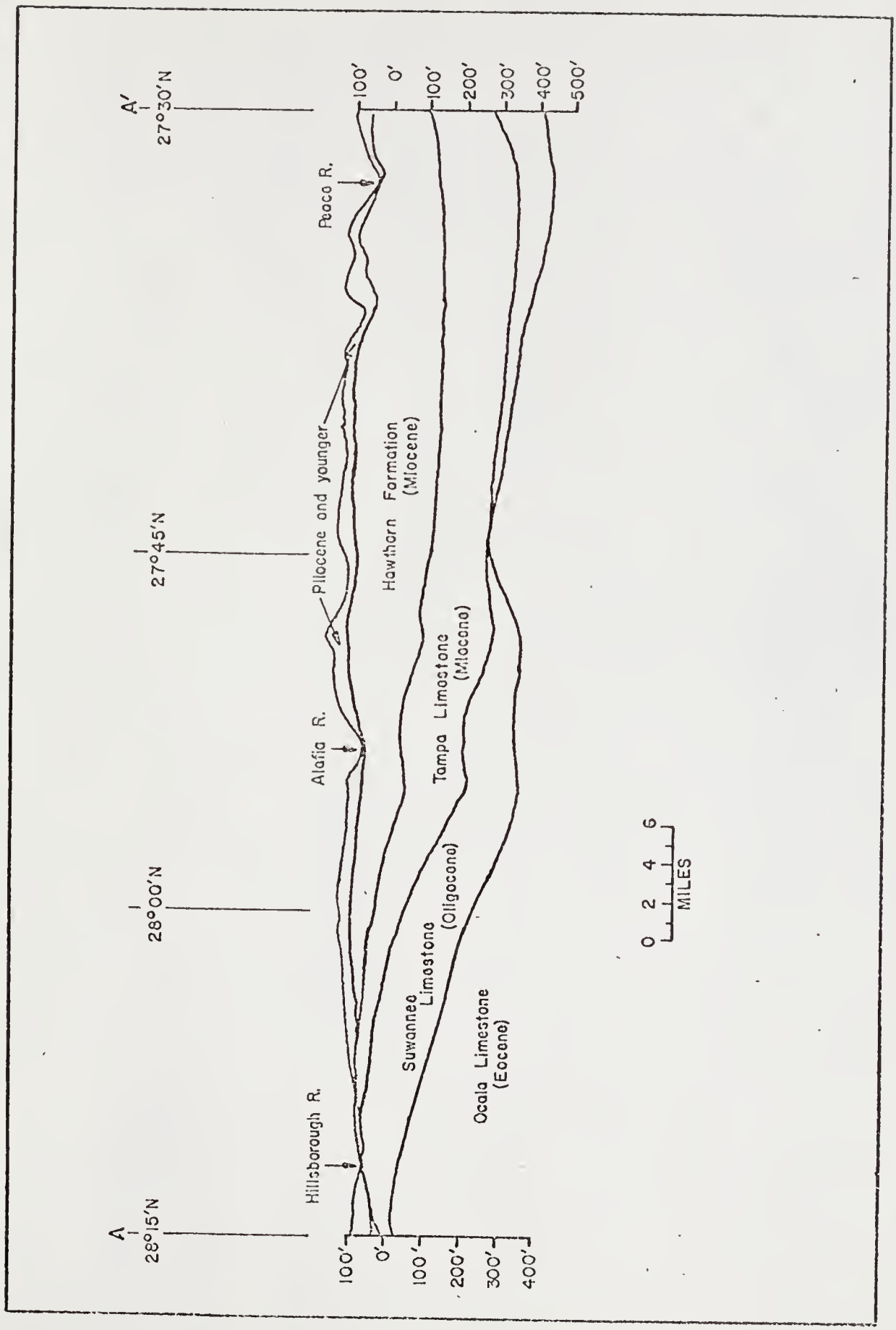

SCALE
0
10
20
MILES
A
HILLSBOROUGH COUNTY
Hillsborough R.
Tampa
Lakeland
POLK COUNTY
Alafia R.
Bartow
Little Manatee R.
Manatee R.
HARDEE COUNTY
Peace R.
MANATEE COUNTY

Figure 6. Cross-section A-A' through land-pebble phosphate district showing general stratigraphy. Location of this section is shown in Fig. 5 (taken from Altschuler et al., 1964).


A
28°15'N
28°00'N
27°45'N
27°30'N
A'
Hillsborough R.
Alafia R.
Pliocene and younger
Peace R.
Ocala Limestone
(Eocene)
Suwannee
Limestone
(Oligocene)
Tampa Limestone
(Miocene)
Hawthorn Formation
(Miocene)
100'
0'
100'
200'
300'
400'
500'
0 2 4 6
MILES

a transgressing sea that flooded an eroded land surface. Cooke (1945) and many others believe that it was deposited over all of what is now Florida and has since been eroded from the Ocala arch. Vernon (1951), however, believes that the Ocala arch was already above sea level during Miocene time and that the Hawthorn formation was never deposited on it. The Hawthorn formation averages 4 to 17% $CaPO_4$ (Carr and Alverson, 1959).

Although there are seven Pliocene age formations in Florida, only the Alachua formation and the Bone Valley formation are of interest here. The Alachua formation is unique in Florida in that it is a terrestrial deposit containing bones of land animals of middle Pliocene age. It always overlies the Ocala limestone, the Hawthorn formation having been leached away (Cooke, 1945). The lower part of the Alachua formation contains phosphate rock (35% P_2O_5) occurring as plates and boulderlike masses. Cooke believed that the phosphate originally occurred as grains in the Hawthorn formation. He stated that the grains were dissolved by downward percolating rain water; when the solution reached the underlying rock, the phosphate was reprecipitated. He believed this process began as soon as the Hawthorn formation emerged from the sea and has continued ever since, although interrupted during the Pleistocene epoch.

The Bone Valley formation, which is the only formation mined today, consists of clayey sand in its upper part and

phosphate particles, sand, clay and gravel in its lower part (Altschuler et al., 1964). It is believed to have been deposited in the broad delta of a stream opening into the ocean with parts being deposited in the open sea. The average P_2O_5 content of the nodules is 35% (Vernon, 1951). The phosphatic portion contains both land and marine vertebrate fossils (Sellards, 1913).

In summary, the oldest stratigraphic unit containing phosphate is the Hawthorn formation (middle Miocene); Pliocene formations deposited on or partially derived from the Hawthorn formation are enriched in phosphorus to the extent of being economically mineable. An explanation for the origin of the phosphorus, then, must account for the phosphorus in the Hawthorn formation as well as that in the mineable rock of later formations.

METHODS

Model Development

From the review of the literature and from conferences with many people concerned with the area under study, preliminary models were developed. These can be written in mathematical language or diagrammed in pictorial representation of flows, storage sites, and process pathways. First, the state variables (stored properties) of the system were listed; these became the storage tanks in the model diagrams. A list of outside energy sources and forces which affect the level of the quantity in the storage tanks was compiled. These became the circular forcing functions of the model diagrams. The storage tanks and forcing functions were connected by lines with the intersection of pathways being some function indicating their interaction. Intersection functions may be additive, multiplicative, exponential, logarithmic, or switching (on or off action). The model building process led to the identification of major pathways and state variables. Then numerical data on magnitudes were obtained from the literature. All numbers refer to some base line year and to the specific area being modeled. Where observed data from the area were unavailable,

numbers for the same process in another similar area were used.

Symbols Used in Model Diagrams

All models are depicted in the energy language developed by H. T. Odum. A description of each symbol and its mathematical meaning can be found in Odum (1971b and 1972). The symbols used in the models in this thesis are pictured and described in Fig. 7. The Peace River estuarine model involved fluid transport of a solute (phosphorus in water). The sensor and other symbols needed for these models developed by H. T. Odum after his original book are included in Fig. 8. In the Peace River estuarine model the sensor was used both with and without a backforce.

Examination of Numbers to Gain Perspective

After each pathway was identified and estimated numerically, it was possible to do an overall budget calculation of the whole system and of unit models within the system. Missing values in some instances were calculated by difference as if the system were in steady state. Associated with each state variable are inflows and outflows so that the budget for the storage was easily calculated. This made possible identification of the relative importance of each pathway. A pathway with a numerical value several orders of magnitude less than others does not exert a major effect

Figure 7. The symbols of the energy circuit language used in this thesis (from Odum, 1971b).

a. Outside source of energy delivering forces according to a program controlled from outside; a forcing function (N).

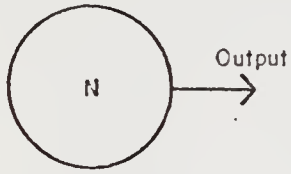
b. A pathway whose flow is proportional to the quantity in the storage or source upstream ($J = kN$). The heat sink represents the energy losses associated with friction and back-forces along pathways of energy flow.

c. A compartment of energy storage within the system storing a quantity as the balance of inflows and outflows ($\dot{Q} = J - kQ$).

d. Multiplicative intersection of two pathways coupled to produce an outflow in proportion to the product of both; control action of one flow on another; limiting factor action; workgate (KN_1N_2).

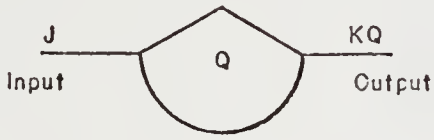
e. A combination of "active storage" and a "multiplier" by which potential energy stored in one or more sites in a subsystem is fed back to do work on the successful processing and work of that unit; autocatalytic ($\dot{Q} = kQ(N - Q/C)$ and many variations.

f. Production and regeneration module (P-R) formed by combining a cycling receptor module, a self-maintaining module which it feeds, and a feedback loop which controls the inflow process by multiplicative and limiting actions. The green plant is one example. On a large scale the module may represent plants and consumers of ecosystems or agriculture and cities.

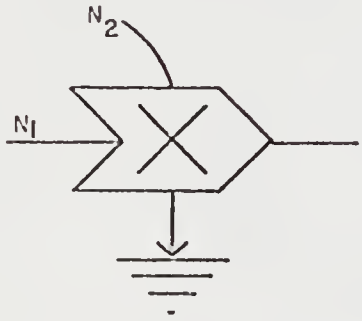


Energy Source
(A)

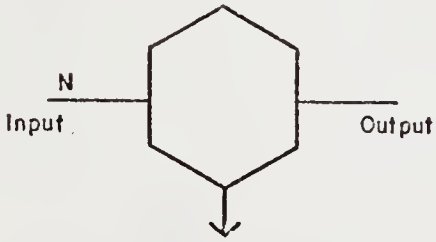
Heatsink
(B)



State Variable
(C)



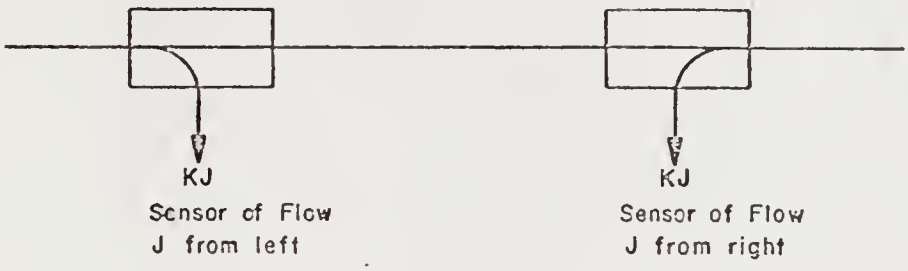
Multiplier Interaction
(D)



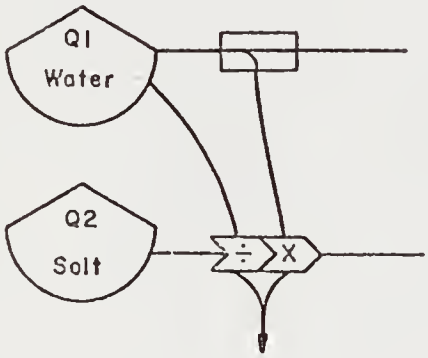
Group Symbol
(Self Maintaining
Consumer Population)
(E)

Group Symbol
(Plant Population)
(F)

Figure 8. Diagrammatic representation and mathematical description of the sensor symbol for use in modeling the fluid transport of a solute, taken from Odum, memorandum number 11, 1972. The sensor delivers a force to a diverging pathway that is proportional to the flow sensed and derives its energy from it.

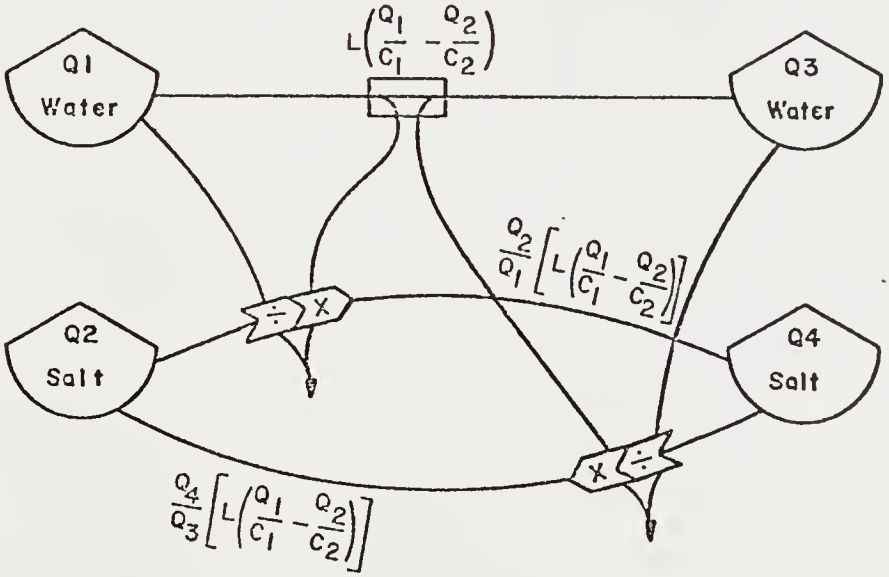


(a)



$$\frac{Q_2}{Q_1} K_1 Q_1 = K_1 Q_2$$

No Backforce
(b)



With Backforce
(c)

on the system, and conversely a pathway several orders of magnitude larger than others is one to be considered carefully since it may be the controlling pathway for the system. To gain further perspective on the importance of pathways, residence times and turnover rates for each state variable were calculated. The residence time is the quantity in the storage divided by the sum of the flows into it, and the turnover rate is the inverse of the residence time. These calculations yielded insight into times involved for change and stability.

Simulation Model

Computer simulation of the entire model developed for each system was not readily done or useful since the models were large. However, at this stage in the methodology, the relative importance of each pathway was estimated, and insight into expected model behavior gained. Then a simplified diagram was developed. It included the pathways and compartments which play a major role in model behavior and which are important for variations to be simulated. A test simulation was made of the simplified model in order to identify unexpected model behavior. Although the whole complexity of the system was not simulated with the simplified model, it represented the essence of the system and identified unexpected complications (e.g., if a state variable decreased when it was expected to increase).

Writing and Scaling Equations

The set of differential equations associated with each system was written directly from the energy language diagram of the system. Each storage or state variable is the integrated sum of the inflows minus the sum of the outflows plus initial conditions. The mathematical terms for each inflowing or outflowing pathway are shown in Figs. 9, 25, and 38 (refer to Odum, 1972, for the theoretical derivation of the mathematics associated with the energy language).

The set of differential equations of the real systems all required magnitude scaling to keep outputs within the range of voltages on the analog computer. In scaling, the values of the voltages in the computer are related to the values of the corresponding dependent variables in the system. Thus, the scale factor is a constant of proportionality which tells how many volts on the computer represent one unit of the corresponding variable in the system. Since the constants chosen for scaling must have a magnitude at least equal to the maximum value of the associated original variable, some knowledge of the maximum values of the variables in the system is required. The numerical coefficients of each of the terms in the equations are transformed into potentiometer settings on the analog computer. These settings may range from 0.001 to 0.999 so that all coefficients must be scaled to fit into this range.

Simulation Procedures

There are advantages and disadvantages to both analog and digital computer simulation procedures. The analog computer allows for continuous rather than step-wise integration and gives the user closer communication with his model; however, the size of the model is limited by the hardware on the computer. Digital simulation has errors if steps are too large, costs more, and takes longer to debug. Both were used in the simulations done here.

Digital Simulation Procedure

The Peace River Estuarine System model was simulated on an IBM 1800 computer. The differential equations were written in Digital Simulation Language (DSL); a language developed for continuous simulations on the 1800 computer. The program was prepared directly from the set of differential equations and utilized a fixed format for input and output. These features greatly simplified the programming and allowed the user to concentrate on the problem rather than on the mechanism for implementing the simulation. The language utilized centralized integration to ensure that all integrator outputs were computed simultaneously at the end of the integration cycle. These simulations utilized fourth order Runge-Kutta integration with a fixed step size. The step size programmed corresponds to one day except during the slime spill when it was one minute for four days. All DSL programs are included in Appendix B.

Analog Simulation Procedure

A submodel of the estuarine mouth of the Peace River System with nitrogen and phosphorus interactions and a geologic time model of phosphorus deposition were simulated on the Electronic Associates, Incorporated, MiniAc analog computer. An analog diagram or program (Appendix B) was written directly from the differential equations and patched onto the MiniAc board.

Experimental Manipulations of Models

Alternative management choices related to man's impact on the system were involved in each model simulation (see discussion). Each issue was tested separately; appropriate calculations to incorporate changes in the numerical values were performed and the model simulated for this variation. The models were used as though controlled experiments had been performed for one factor at a time.

RESULTS AND DISCUSSION

Phosphorus in the Peace River - Charlotte Harbor Estuarine System

Data Evaluation

The simplified model for the Peace River system is given in Fig. 9. Included are the mathematical terms for each source, storage, and flow. Figure 10 is the same diagram showing the numerical values calculated in Table 3 using data obtained from the literature. Table 3 describes the parameter defined, gives its numerical value and the source for the number. Notes found in Appendix A describe in detail the derivation of each numerical value.

Since the large model represented in Fig. 10 is difficult to conceptualize, the relative magnitude of the flows of water and of phosphorus into the river mouth (into Q_4 and Q_5) are shown in summary diagrammatic form (Fig. 11).

Note that the river flow, mining water, and tidal input are all the same order of magnitude (Fig. 11a). Sewage effluent is less by two orders of magnitude and water from a slime spill is higher by one order of magnitude. Note that mining water is a significant percentage of the river flow (26% when the river is at intermediate

Figure 9. Simplified model of the Peace River - Charlotte Harbor estuarine system with the mathematical terms for the sources, storages, and fluxes indicated.

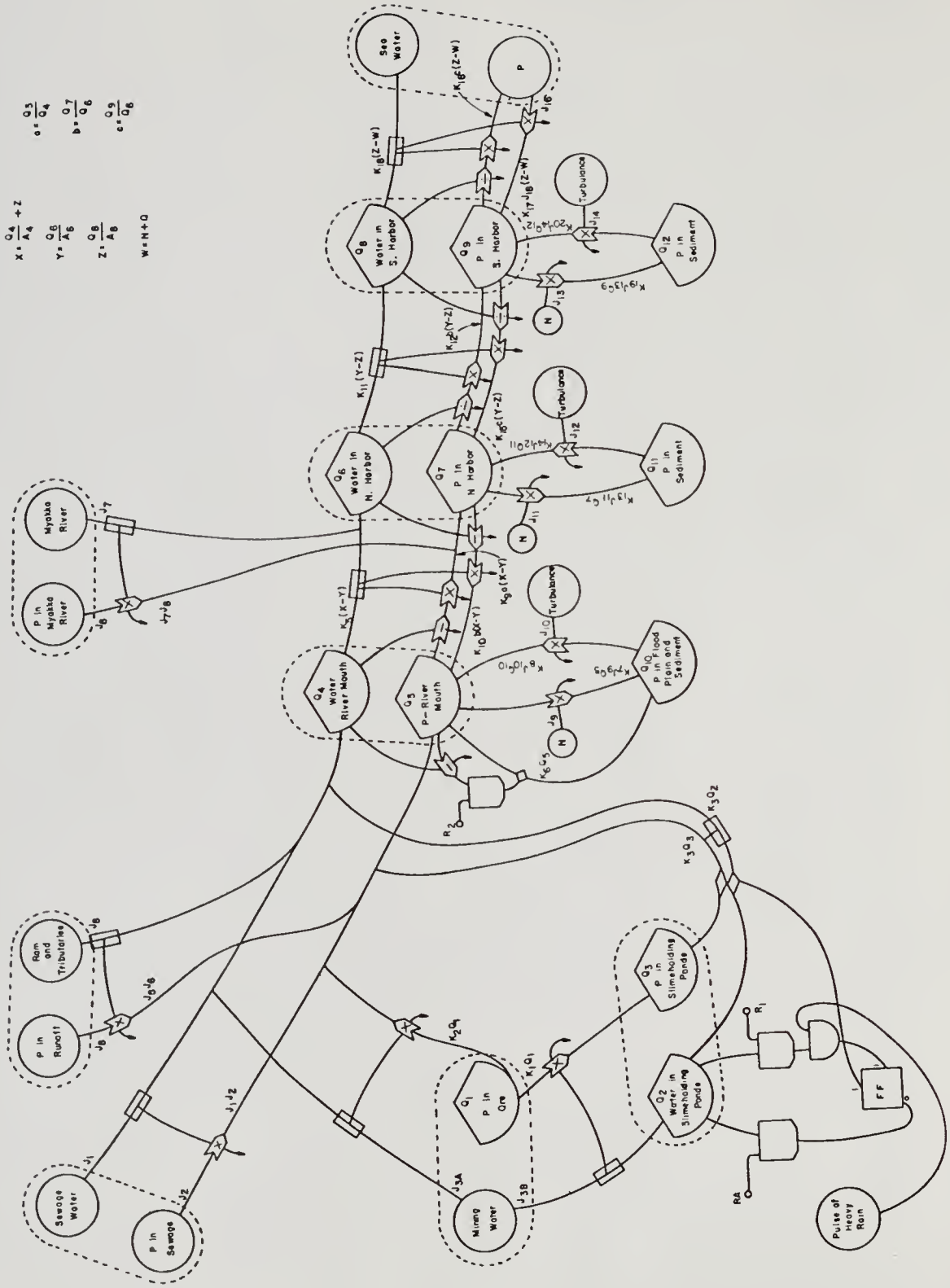

Sea Water
P
Turbulance
Turbulance
Turbulance
Turbulance
Q8 Water in S. Harbor
Q9 P in S. Harbor
Q12 P in Sediment
Q6 Water in N. Harbor
Q7 P in N Harbor
Q11 P in Sediment
Q4 Water River Mouth
Q5 P- River Mouth
Q10 P in Flood Plain and Sediment
Myaka River
P in Myaka River
Ram and Tributaries
P in Runoff
Sewage Water
P in Sewage
Mining Water
Q1 P in Ore
Q3 P in Slimeholding Ponds
Q2 Water in Slimeholding Ponds
FF
Pulse of Heavy Rain
N
N
N
N
R1
R2
RA

Figure 10. Model from Fig. 9 of the Peace River - Charlotte Harbor estuarine system, with the numerical values for the sources, storages, and fluxes indicated. Units are g/m^3 for phosphorus concentrations, 10^6 m^3/day for water flow, and 10^6 g/day for phosphorus flow.

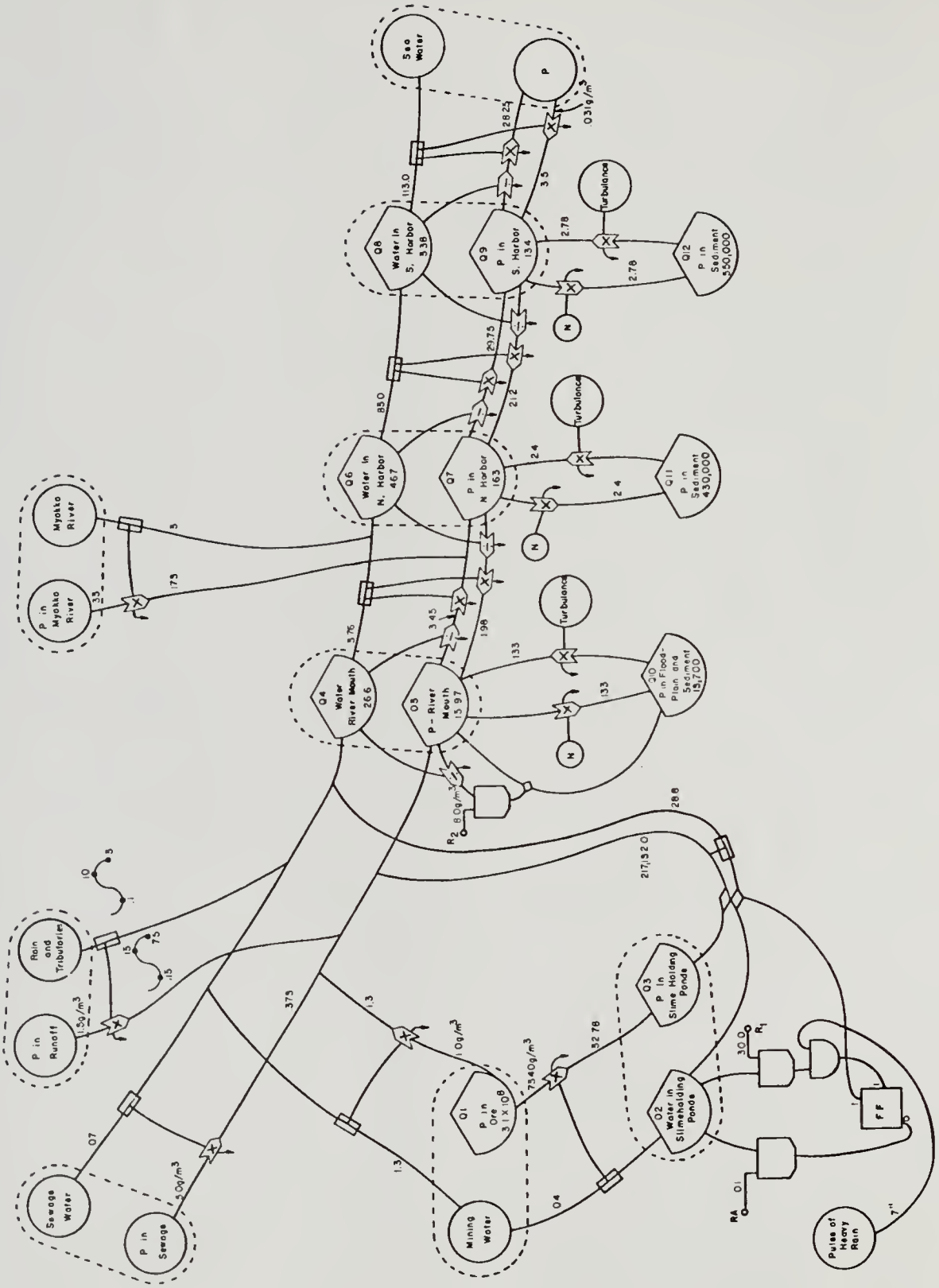

Sea Water
P
Turbulance
Q8 Water in S. Harbor 338
Q9 P in S. Harbor 134
Q12 P in Sediment 550,000
Turbulance
Q6 Water in N. Harbor 467
Q7 P in N Harbor 163
Q11 P in Sediment 430,000
Turbulance
Q4 Water River Mouth 266
Q5 P- River Mouth 1597
Q10 P in Flood-Plain and Sediment 15,700
Myakka River
P in Myakka River
Rain and Tributaries
P in Runoff
Sewage Water
P in Sewage
Mining Water
Q1 P in Ore 3.1X10^8
Q3 P in Slime Holding Ponds
Q2 Water in Slimeholding Ponds
Pulse of Heavy Rain
FF
N
N
N
R1
R2
RA
0.31g/m^3
1.59g/m^3
5.00g/m^3
7340g/m^3
8.0g/m^3

Table 3

Sources, Storages, and Rates for the
Peace River - Charlotte Harbor Estuarine System (Figs. 9 and 10)

Parameter	Note (Appendix A)	Description	Numerical Value	Source
Q_1	1	Phosphorus remaining in the ore in Florida	3.10×10^{14} g	Mansfield (1942)
$(Q_2=R_1)$	2	Water stored in the slime holding pond	3.0×10^{7} m^3	Harriss et al. (1972) Specht (1950)
Q_3	3	Phosphorus stored in slime holding pond	7,540 g/m^3	Toler (1967)
Q_4	4	Water in Peace River Mouth	2.66×10^{7} m^3	U.S. Coast and Geodetic Survey Map (1971)
Q_5	5	Phosphorus in Peace River Mouth	1.597×10^{7} g (.6 mg/1)	Alberts et al. (1970)
Q_6	6	Water in northern section of Charlotte Harbor	4.67×10^{8} m^3	U.S. Coast and Geodetic Survey Map (1971)
Q_7	7	Phosphorus in northern section of Charlotte Harbor	1.63×10^{8} g (.35 mg/1)	Alberts et al. (1970)
Q_8	8	Water in southern section of Charlotte Harbor	5.38×10^{8} m^3	U.S. Coast and Geodetic Survey Map (1971)

Table 3 (continued)

Parameter	Notes (Appendix A)	Description	Numerical Value	Source
Q_9	9	Phosphorus in southern section of Charlotte Harbor	1.34×10^8 g (.25 mg/1)	Alberts et al. (1970)
Q_{10}	10	Phosphorus in sediments and floodplain of Peace River Mouth	1.57×10^{10} g 6" deep	Huang and Goodell (1967)
Q_{11}	11	Phosphorus in sediments of northern section of Charlotte Harbor	4.3×10^{11} g 6" deep	Huang and Goodell (1967)
Q_{12}	12	Phosphorus in sediments of southern section of Charlotte Harbor	5.5×10^{11} g 6" deep	Huang and Goodell (1967)
J_1	13	Sewage water entering the Peace River	7.54×10^4 m^3/day	Inventory of Sewerage Systems in Fla.(1966)
J_2	14	Phosphorus in sewage entering the river	5.0 g/m^3	Am. Chemical Society (1969)
J_{3A}	15	Water from mining operations entering river	1.3×10^6 m^3/day	Lanquist (1953) Specht (1950)
J_{3B}	16	Water from mining operations entering an average slime pond	41.7×10^3 m^3/day	Specht (1950)

Table 3 (continued)

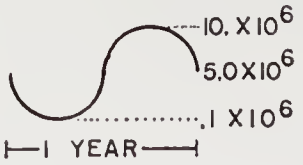
Parameter	Notes (Appendix A)	Description	Numerical Value	Source
J_4	17	Pulse of heavy rain required for a slime spill	7 inches/day	Specht (1950)
J_5	18	Primary river flow resulting from rain and tributaries		Dragovich et al. (1968) U.S. Geol. Surv. (1961-1968)
J_6	19	Phosphorus content of primary river flow	1.5 g/m^3	U.S. Geol. Surv. (1968)
J_7	20	Myakka River discharge	5.0×10^5 m^3/day	Dragovich et al. (1968)
J_8	21	Phosphorus content of Myakka River	.35 g/m^3	Dragovich et al. (1968)
J_9	22	Factors affecting precipitation of phosphorus in the river mouth	.152 g/m^3	U.S. Geol. Surv. (1968)
J_{10}	23	Turbulence causing phosphorus to redissolve into surface waters from sediment	56.16×10^9 kilocal/day	Estimate of potential energy of tide
J_{11}	24	Factors affecting precipitation of phosphorus in the northern harbor	.018 g/m^3	Alberts et al. (1970)

Table 3 (continued)

Parameter	Note (Appendix A)	Description	Numerical Value	Source
J_{12}	25	Turbulence in northern section of Charlotte Harbor	95.76×10^{10} kilocal/day	Estimate of potential energy of tide
J_{13}	26	Factors affecting precipitation of phosphorus in the southern harbor	.018 g/m^3	Alberts et al. (1970)
J_{14}	27	Turbulence in southern section of Charlotte Harbor	166.5×10^{10} kilocal/day	Estimate of potential energy of tide
J_{15}	28	H = mean tidal range		U.S. Dept. of Commerce (1972)
J_{16}	29	Phosphorus in sea water	.031 mg/1	Graham et al. (1954)
$K_1Q_1J_{3B}$	30	= J_{3C}, flux of phosphorus in ore to phosphorus in the slime holding ponds	7,540 g/m^3	Toler (1967) Specht (1950)
$K_2Q_1J_{3A}$	31	= J_{3D}, flux of phosphorus to river from mining operations	1.0 g/m^3	Lanquist (1953)
K_3Q_2	32	Water released to Peace River when dam breaks	2.88×10^7 m^3/day	Specht (1950) Harriss et al. (1970)
K_3Q_3	33	Phosphorus released to river when dam breaks	2.1715×10^{11} g/day	Toler (1967)

Table 3 (continued)

Parameter	Note (Appendix A)	Description	Numerical Value	Source
$K_5 \left[\left(\frac{Q_4}{A_4} + Z \right) - \frac{Q_6}{A_6} \right]$	34	Flux of water in and out of river mouth	5.76×10^6 m^3/day	U.S. Coast and Geodetic Survey Map (1971)
$K_6 Q_5$	35	Flux of phosphorus to sediment when the river load exceeds its capacity (usually when a slime spill occurs)	2.10×10^{11} g/day	Harriss et al. (1972)
$K_7 J_9 Q_5$	36	Flux of phosphorus from surface water to sediments in river mouth	1.33×10^5 g/day	Harriss et al. (1972) Pomeroy et al. (1972)
$K_8 J_{10} Q_{10}$	37	Flux of phosphorus from sediments to surface water in river mouth	1.33×10^5 g/day	Harriss et al. (1972) Pomeroy et al. (1972)
$K_9 \frac{Q_5}{Q_4} \left[\left(\frac{Q_4}{A_4} + Z \right) - \frac{Q_6}{A_6} \right]$	38	Flux of phosphorus out of the river mouth	3.456×10^6 g/day	Alberts et al. (1970)
$K_{10} \frac{Q_7}{Q_6} \left[\left(\frac{Q_4}{A_4} + Z \right) - \frac{Q_6}{A_6} \right]$	39	Flux of phosphorus into the river mouth	1.98×10^6 g/day	Alberts et al. (1970)

Table 3 (continued)

Parameter	Note (Appendix A)	Description	Numerical Value	Source
$K_{11}\left(\frac{Q_6}{A_6}-\frac{Q_8}{A_8}\right)$	40	Flux of water in and out of northern section of Charlotte Harbor with tides	85.0×10^6 m^3/day	U.S. Dept. of Commerce (1972) U.S. Coast and Geodetic Survey Map (1971)
$K_{12}\frac{Q_7}{A_6}\left(\frac{Q_6}{A_6}-\frac{Q_8}{A_8}\right)$	41	Flux of phosphorus out of northern section of Charlotte Harbor	2.975×10^7 g/day	Alberts et al. (1970)
$K_{13}J_{11}Q_7$	42	Flux of phosphorus from surface water to sediments in northern section of harbor	2.4×10^6 g/day	Alberts et al. (1970)
$K_{14}J_{12}Q_{11}$	43	Flux of phosphorus from sediment to surface water	2.4×10^6 g/day	Alberts et al. (1970)
$K_{15}\frac{Q_9}{Q_8}\left(\frac{Q_6}{A_6}-\frac{Q_8}{A_8}\right)$	44	Flux of phosphorus into northern section of Charlotte Harbor	2.12×10^7 g/day	Alberts et al. (1970)
$K_{16}\left(\frac{Q_8}{A_8}-(H+D)\right)$	45	Flux of water in and out of the southern harbor through Boca Grande Pass	1.13×10^8 m^3/day	O'Brien (1969)

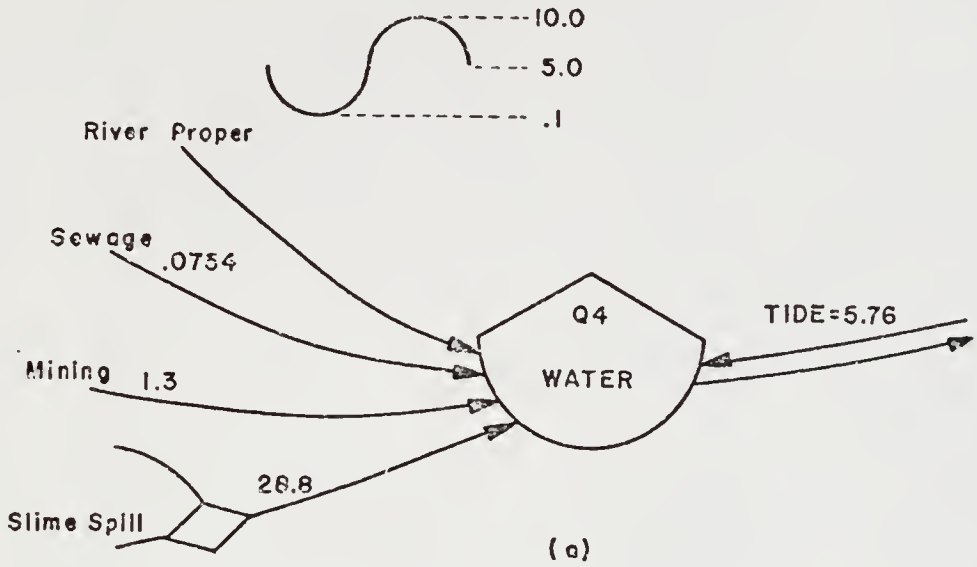
Table 3 (continued)

Parameter	Note (Appendix A)	Description	Numerical Value	Source
$K_{17}J_{16}\left\{\frac{Q_8}{A_8}-(H+D)\right\}$	46	Flux of phosphorus into the lower harbor through Boca Grande Pass	3.50×10^6 g/day	Graham et al. (1954)
$K_{18}\frac{Q_9}{Q_8}\left\{\frac{Q_8}{A_8}-(H+D)\right\}$	47	Flux of phosphorus out of the lower harbor through Boca Grande Pass	2.825×10^7 g/day	Alberts et al. (1970)
$K_{19}J_{13}Q_9$	48	Flux of phosphorus from surface water to sediment in southern section of harbor	2.78×10^6 g/day	Alberts et al. (1970)
$K_{20}J_{14}Q_{12}$	49	Flux of phosphorus from sediments to surface water	2.78×10^6 g/day	Alberts et al. (1970)

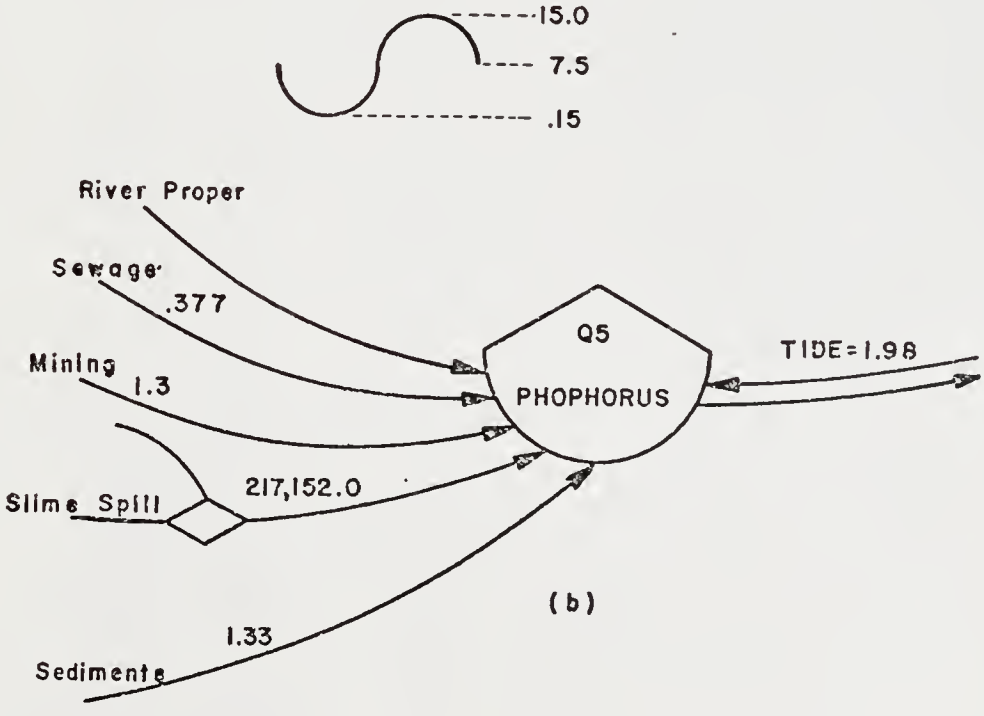
Figure 11. Summary models for a unit area.

a. Flux of water into the Peace River Mouth; units are 10^6 m^3/day.

b. Flux of phosphorus into the Peace River Mouth; units are 10^6 g/day.


10.0
5.0
.1
River Proper
Sewage
.0754
Mining
1.3
Slime Spill
28.8
Q4
WATER
TIDE=5.76

(a)


15.0
7.5
.15
River Proper
Sewage
.377
Mining
1.3
Slime Spill
217,152.0
1.33
Sediments
Q5
PHOPHORUS
TIDE=1.98

(b)

flow). When a slime spill occurs, the water discharged into the river greatly increases; the data indicate river discharge approximately doubles.

With similar considerations in mind, note the relative magnitude of the phosphorus flows into the river mouth (Fig. 11b) from rivers and tide.

Clearly, the total phosphorus contribution of each source to the river is dependent not only on the phosphorus concentration but also on the amount of water from the source. For example, except for slime pond water, sewage effluent has the highest concentration (5 g/m^3). However, phosphorus contribution to the river from sewage is the smallest of all flows. On the other hand, tidal water which enters the river mouth with a flood tide has a relatively low concentration (0.35 g/m^3) but the tide contributes a significant amount of phosphorus to the system. In the first case small amounts of water are involved and in the second case large amounts of water enter with the tide. Except during the dry season the river proper, whose phosphorus comes from the natural drainage of the Peace River system (approximately 1,400 mi^2, Lanquist, 1953), is the major phosphorus contributor.

Phosphorus in mining water, in the drainage water proper, and in the flood tide input is the same order of magnitude. Contributions from sewage and sediments are one order of magnitude smaller while, if a dam break with a corresponding

slime spill occurs, the contribution of phosphorus is five orders of magnitude larger than all other contributors.

The phosphorus contribution of the Myakka River (Fig. 10) to the northern part of Charlotte Harbor is also one order of magnitude less than the flows from major outside sources.

As calculated for the amount of phosphorus in and out of the sediments, the model is in steady state unless a slime spill occurs so that no net erosion or deposition takes place.

Residence times for each estuarine storage were calculated by dividing the quantity in the storage by the sum of all flows entering the storage ($Q/\Sigma J$). Turnover rates are the inverse. The results are given in Table 4. All the residence times are similar (three to six days) except the phosphorus in sediments, most of which is inactive.

Simulation Evaluation

Figure 9 depicts the mathematical terms which represent each storage and flux in the system. Differential equations needed for a simulation of the system are written directly from this diagram (Fig. 12).

Table 4

Residence and Turnover Times for the Storages of the Peace River - Charlotte Harbor System

Storage (m^3 or g)	Residence Times (days)	Turnover Rate (per day)
Water in Peace River Mouth (Q_4)		
Low Flow	3.67	0.27
Phosphorus in Peace River Mouth (Q_5)		
Low Flow	4.05	0.25
Water in northern Charlotte Harbor (Q_6)	5.12	0.19
Phosphorus in northern Charlotte Harbor (Q_7)	5.98	0.17
Water in southern Charlotte Harbor (Q_8)	2.7	0.37
Phosphorus in southern Charlotte Harbor (Q_9)	3.7	0.27
Phosphorus in floodplain of river mouth (Q_{10})	118,045.0	8.47×10^{-6}
Phosphorus in sediment of Northern Harbor (Q_{11})	179,166.0	5.58×10^{-6}
Phosphorus in sediment of Southern Harbor (Q_{12})	197,841.0	5.05×10^{-6}

$x = Q_4/A_4 + z$ $\qquad a = Q_5/Q_4$

$y = Q_6/A_6$ $\qquad b = Q_7/Q_6$

$z = Q_8/A_8$ $\qquad c = Q_9/Q_8$

$w = H+D$

$$\dot{Q}_1 = -k_1 Q_1 J_{3B} - k_2 Q_1 J_{3A}$$

$$\dot{Q}_2 = J_{3B} - \overbrace{k_3 Q_2}^{\text{if } Q_2 > R_1 \text{ and } J_4 > 7}$$

$$\dot{Q}_3 = k_1 Q_1 J_{3B} - \overbrace{k_3 Q_3}^{\text{if } Q_2 > R_1 \text{ and } J_4 > 7}$$

$$\dot{Q}_4 = J_1 + J_{3A} + J_5 - k_5 (x-y) + \overbrace{k_3 Q_2}^{\text{if } Q_2 > R_1 \text{ and } J_4 > 7}$$

$$\dot{Q}_5 = J_1 J_2 + J_5 J_6 + k_2 Q_1 J_{3A} - k_7 J_9 Q_5 + k_8 J_{10} Q_{10} - \overbrace{k_9 a(x-y)}^{\text{if } y<x} - \overbrace{k_{10} b(x-y)}^{\text{if } y>x} + \overbrace{k_3 Q_3}^{\text{if } Q_2 > R_1 \text{ and } J_4 < 7} - \overbrace{k_6 Q_5}^{\text{if } a > R_2}$$

$$\dot{Q}_6 = J_7 + k_5 (x-y) - k_{11} (y-z)$$

$$\dot{Q}_7 = J_7 J_8 + \overbrace{k_9 a(x-y)}^{\text{if } y<x} + \overbrace{k_{10} b(x-y)}^{\text{if } y>x} - \overbrace{k_{12} b(y-z)}^{\text{if } z<y} - \overbrace{k_{15} c(y-z)}^{\text{if } z>y} - k_{13} J_{11} Q_7 + k_{14} J_{12} Q_{11}$$

$$\dot{Q}_8 = k_{11} (y-z) - k_{16} (z-w)$$

Figure 12. Differential equations.

$$\dot{Q}_9 = \overbrace{k_{12}b(y-z)}^{\text{if } z<y} + \overbrace{k_{15}c(y-z)}^{\text{if } z>y} - \overbrace{k_{17}J_{16}(z-w)}^{\text{if } w>z} - \overbrace{k_{18}c(z-w)}^{\text{if } w<z}$$

$$-k_{19}J_{13}Q_9 + k_{20}J_{14}Q_{12}$$

$$\dot{Q}_{10} = k_7J_9Q_5 - k_8J_{10}Q_{10} + \overbrace{k_6Q_5}^{\text{if } a>R_2}$$

$$\dot{Q}_{11} = k_{13}J_{11}Q_7 - k_{14}J_{12}Q_{11}$$

$$\dot{Q}_{12} = k_{19}Q_9J_{13} - k_{20}J_{14}Q_{12}$$

Figure 12. (continued)

The computer program in Digital Simulation Language (DSL) for the entire set of differential equations is found in Appendix B. That simulation takes out the daily tidal effects and assumes mean low tide for all values (Appendix B). All programs with corresponding data changes for the simulation variations are found in Appendix B.

Results of the digital simulation for five years are shown in graphical form in Figs. 13, 15 and 16. Figure 13 depicts the water, the total phosphorus, and phosphorus concentration in the Peace River Mouth. Note that steady state was immediately attained and continued. The fluctuations in quantity of water (Fig. 13a) in the river mouth correlated in shape directly with the sine wave input (Fig. 11a). Huang and Goodell (1967), Dragovich et al. (1968) and the USGS Water Resources Data for Florida - Surface Water Records (1964-1968) all give Peace River discharge data which indicate maximum discharge in August and September as the simulation showed; however, the literature indicated a second, less significant peak in January and February. The water in the river mouth rises and falls with the order of magnitude shown in the simulation; however, there is a second high in January and February. During the period of maximum flow the model predicted a depth (volume/area) for the river mouth of 5.16 meters ($9.2 \times 10^7 m^3 / 1.78 \times 10^7 m^2$) or 16.5 feet, and at low flow a depth of 2.35 meters ($4.2 \times 10^7 m^3 / 1.78 \times 10^7 m^2$) or 7.55 feet was predicted. These

Figure 13. Simulation results of the model in Figs. 9 and 10 for the Peace River Mouth sector (Q_4 and Q_5). Phosphorus concentration is total P. The surface area included is 1.78×10^7 m^2.

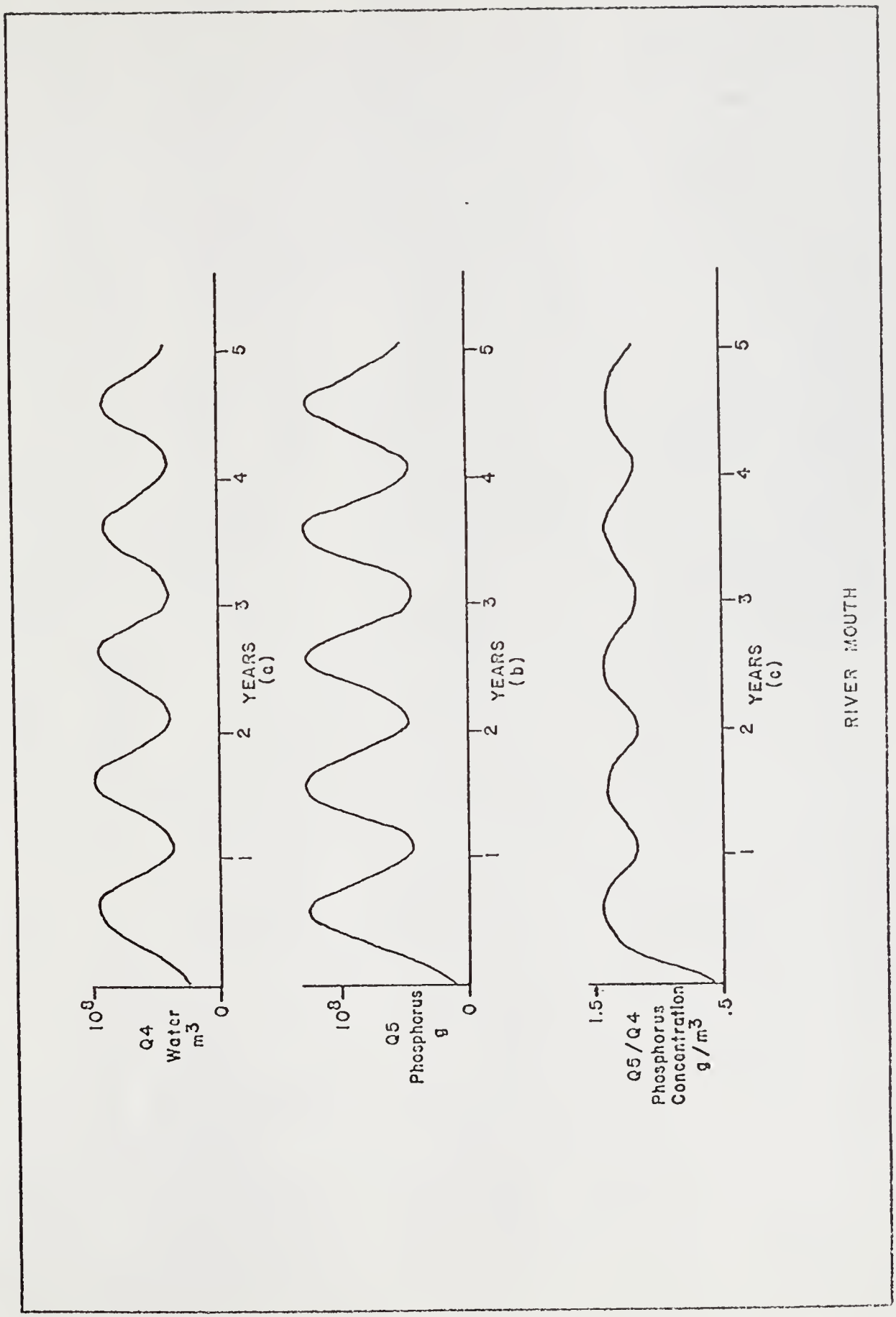

10^8
Q4
Water
m^3
0
1
2
YEARS
(a)
3
4
5
10^8
Q5
Phosphorus
g
0
1
2
YEARS
(b)
3
4
5
1.5
Q5/Q4
Phosphorus
Concentration
g/m^3
.5
1
2
YEARS
(c)
3
4
5
RIVER MOUTH

Figure 14. Graphical representation of the dissolved inorganic phosphorus data obtained by the USGS Water Resources Division in Florida for the Peace River at Arcadia, Florida, shown for four years. It is believed that on the average this represents 90% (see text) of the total phosphorus.

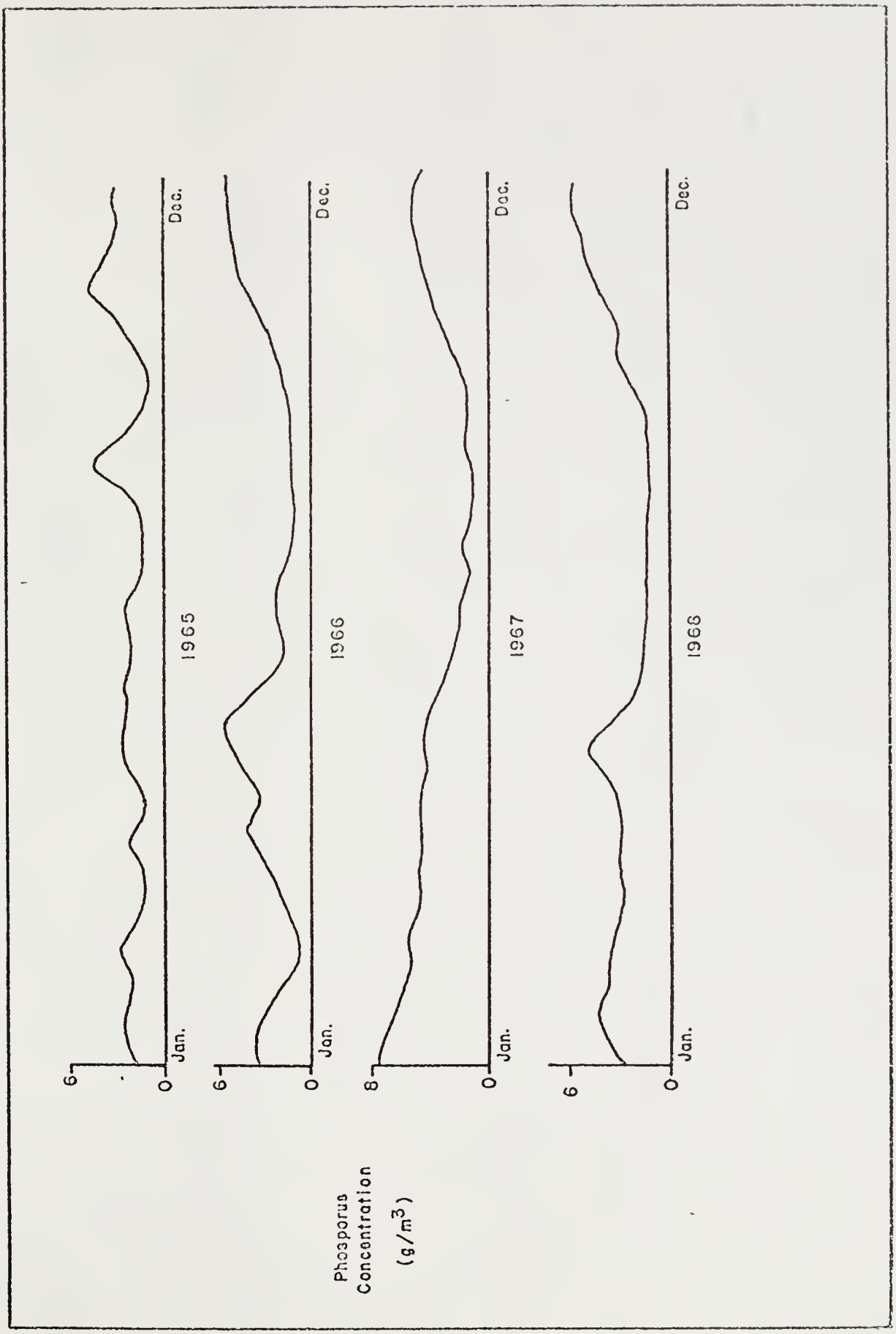

Phosporus
Concentration
(g/m³)
6
0
Jan.
Dec.
1965
6
0
Jan.
Dec.
1966
8
0
Jan.
Dec.
1967
6
0
Jan.
Dec.
1968

Figure 15. Simulation results of the model in Figs. 9 and 10 for the northern Charlotte Harbor sector (Q_6 and Q_7). The surface area included is 1.468×10^8 m^2.

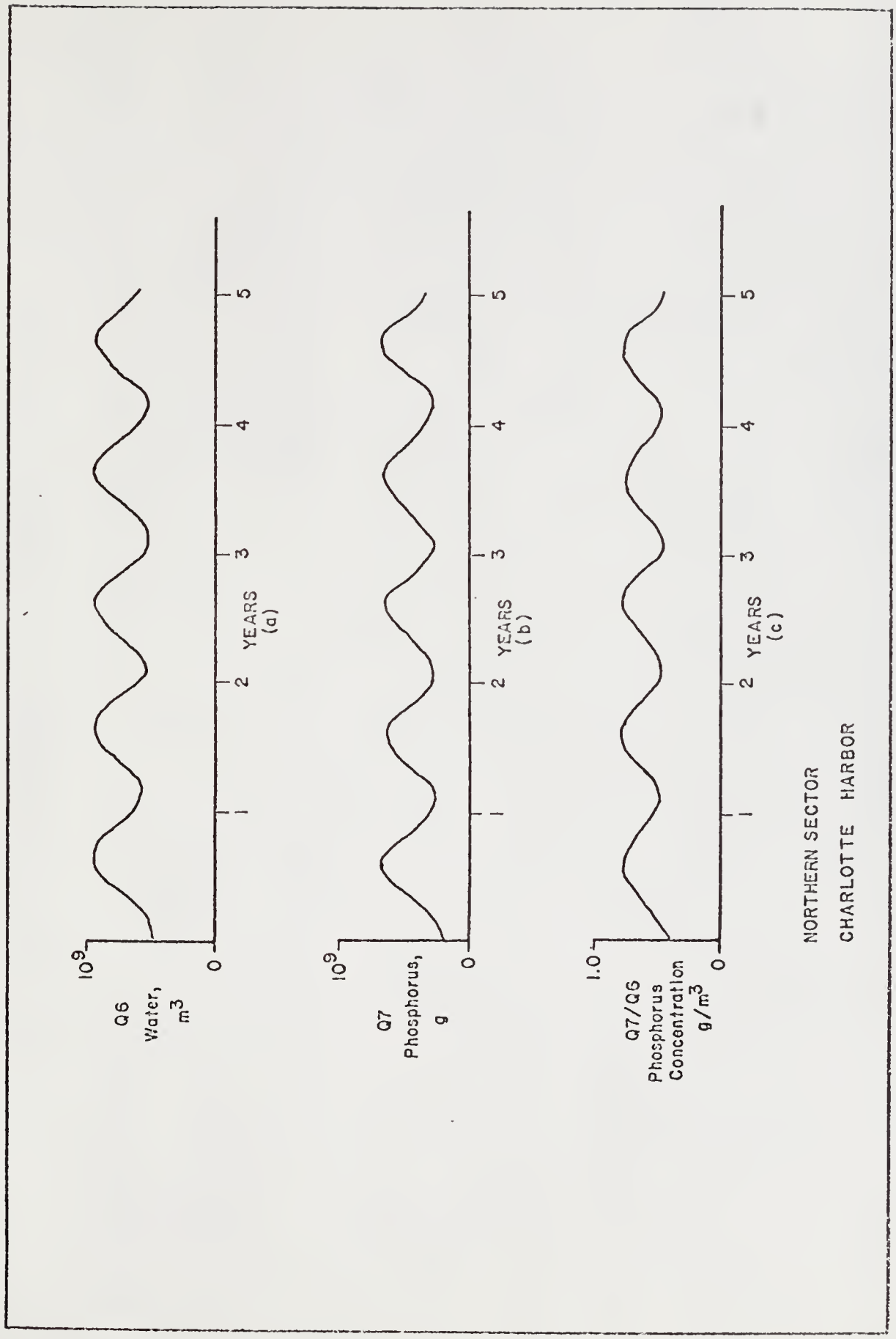
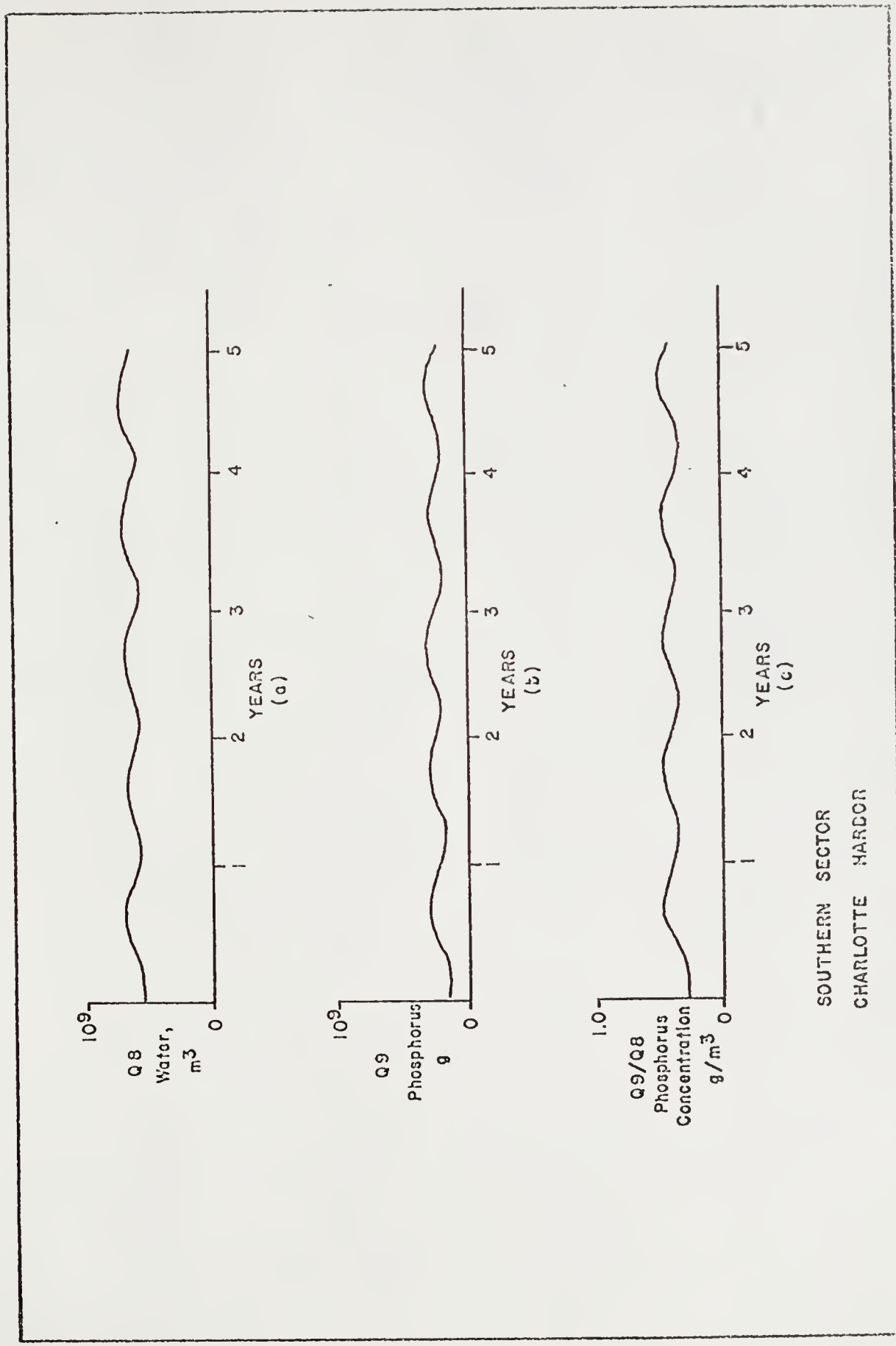

Q6
Water,
m^3
10^9
0
1
2
3
4
5
YEARS
(a)
Q7
Phosphorus,
g
10^9
0
1
2
3
4
5
YEARS
(b)
Q7/Q6
Phosphorus
Concentration
g/m^3
1.0
0
1
2
3
4
5
YEARS
(c)
NORTHERN SECTOR
CHARLOTTE HARBOR

Figure 16. Simulation results of the model in Figs. 9 and 10 for the southern Charlotte Harbor sector (Q_8 and Q_9). The surface area included is 1.871×10^8 m^2.


Q8
Water,
m3
10^9
0
1
2
3
4
5
YEARS
(a)
Q9
Phosphorus
g
10^9
0
1
2
3
4
5
YEARS
(b)
Q9/Q8
Phosphorus
Concentration
g/m3
1.0
0
1
2
3
4
5
YEARS
(c)
SOUTHERN SECTOR
CHARLOTTE HARBOR

values agree well with depths given on the U.S. Coast and Geodetic survey map, 1971.

The fluctuations in quantity of phosphorus in the Peace River mouth (Fig. 13b) correlated in shape directly with the sine wave input (Fig. 11b). The simulation indicated that the total quantity of phosphorus in the river mouth depended largely on the total volume of water present. In support of this is the statement from Dragovich et al. (1968), "the quantity of nutrients contributed by the river to the sea is determined largely by the volume of river flow, not by actual concentrations of nutrients. The maximum amount of phosphorus is discharged in August and September when maximum runoff occurs."

The amplitude of fluctuation in phosphorus concentration (Fig. 13c) was considerably less than fluctuations in total water volume or total phosphorus (Figs. 13a and 13b). This flatter curve implies that input concentrations are staying relatively constant while volume of water varies, which is the case. The curve is flat except for dips in concentration during the dry season. The curve is shaped in this manner because the main contributor of phosphorus except during the dry season was the water draining the region (river proper) which was high in total phosphorus (1.5 g/m^3). During the dry season the major water flow came from mining operations at a concentration of 1.0 g/m^3. The result was that the overall concentration drops. This

result does not correspond exactly to the data given by Dragovich et al. (1968) or the data in the USGS Water Resources Data for Florida publications. These sources indicated that fluctuations in concentration were more severe; however, their data indicated that concentrations were high for a longer period of the year than they were low, and they were low during the dry season. Figure 14 is a graph of dissolved phosphorus concentration for four years as given in the USGS Water Resources Data for Florida at Arcadia, Florida, fifteen miles north of the portion of the river under study. Concentrations of total phosphorus indicated for the river mouth by the simulation ranged from 1.13 g/m^3 to 1.39 g/m^3. Alberts et al. (1970) stated that 90% of the phosphorus in the area was dissolved and found an average concentration of 0.6 g/m^3 dissolved phosphorus which, assuming it represents 90% of the total phosphorus, is lower than that predicted by the simulation. However, total phosphorus was not measured. The USGS data at Arcadia (Fig. 14) were higher than those predicted by the simulation. Dragovich et al. (1968) obtained an average total phosphorus concentration for the river mouth of 0.93 g/m^3 which agrees quite well with the simulation prediction. John F. Dequine of the Southern Fish Culturists, Inc. (personal communications), found inorganic P values for the river mouth ranging from 0.233 to 3.27 mg/1 P. The average value was 1.9 mg/1 P.

Dequine's values also agree well with those predicted by the simulation.

Figure 15 shows the simulation results for water, total phosphorus, and total phosphorus concentration in the northern sector of Charlotte Harbor. Similar seasonal fluctuations in water volume and total phosphorus with river discharge were observed, but the amplitude of the seasonal change was less than that in the river mouth. This was the expected result due to the dampening effect of the tide and the larger area in the harbor over which the river discharge was spread. The volume of water present (Fig. 15a) during the dry season predicted an average depth (volume/area) of 3.4 meters ($5.0 \times 10^8 m^3 / 1.468 \times 10^8 m^2$) or 10.9 feet. During maximum river discharge period depth was 6.1 meters ($9 \times 10^8 m^3 / 1.468 \times 10^8 m^2$) or 19.6 feet. These depths agree well with those given on the U.S. Coast and Geodetic survey map (1971).

The graph of phosphorus concentration in the northern sector of the harbor (Fig. 15c) was not as flat as it was for the river mouth but followed more closely the shape of a sine wave. The larger tidal input of total phosphorus in this area predominated over fluctuations farther up the river. Concentration during the low water volume period was 0.45 g/m^3 and during the high water volume period was 0.75 g/m^3. These values are somewhat higher than those reported as dissolved phosphorus by Alberts et al. (1970);

the maximum values reported there were about 0.5 g/m^3 and the average is 0.35 g/m^3.

Note that all three graphs of Fig. 15 show a time lag between minimum and maximum points for this area relative to the up river area given in Fig. 13. The lag was about 7 days.

Figure 16 has the simulation results for the southern sector of Charlotte Harbor. Seasonal fluctuations in water volume and total phosphorus were greatly dampened by the large tidal effect. Simulation graphs indicated a depth for the harbor at the low volume period of 2.9 meters ($3.5x10^8m^3/1.871x10^8m^2$) or 9.3 feet. At maximum volume period the depth is 3.47 meters ($6.5x10^8m^3/1.871x10^8m^2$) or 11.1 feet. These depths agree well with the U.S. Coast and Geodetic survey map (1971).

The graph depicting phosphorus concentrations in the southern sector of the harbor (Fig. 16c) indicated little seasonal change in concentration. Minimum concentration was 0.3 g/m^3 and maximum was 0.41 g/m^3. These values were slightly higher than the average value of 0.25 g/m^3 for dissolved phosphorus found by Alberts et al. (1970). There is no question, however, that the phosphorus concentrations of Peace River water did affect the entire southern sector of the harbor. Alberts et al. (1970, p. 9) stated,"the wedge of high phosphorus Peace River water maintains its integrity to Boca Grande Pass."

The time lag in the minimum and maximum was seven days from the northern sector of the harbor to the southern sector and fourteen days from the river mouth to the southern sector.

Graphs for the total phosphorus in sediment storages (Q_{10}, Q_{11}, Q_{12}) are not given since the values remained constant at the initial conditions throughout the simulation. Huang and Goodell (1967) stated that no net deposition or erosion has taken place in the harbor for at least the last 100 years. In the river mouth there was evidence that net deposition due to slime spills (Harriss, 1972) has taken place (see discussion following, page 94); however, for the purpose of initial modeling a steady state was assumed and the simulation indicated the same.

With the hope of gaining some insight into the effects of increased pollution pressures in the area which may arise as population increases in South Florida, four variations of the simulation were run: adding nitrogen flux, reducing mining effluent, increasing sewage, and following a surge from a slime pond dam break.

Deposition of Phosphorus in Sediments

Several factors including a nitrogen increase or increased pH could cause deposition of phosphorus in the sediments of the estuary. Pathways J_9, J_{11}, and J_{13} of Fig. 9 pump phosphorus into sediment.

Total dissolved nitrogen concentrations were low in the estuary ranging from .1 mg/l (Connell and Associates, 1972) to .34 mg/l (Odum et al., 1955). High phosphorus may stimulate organic use of nitrogen, keeping it low. As a result, nitrogen may be an important factor in limiting phytoplankton in the presence of high dissolved phosphorus concentrations. If, in the future, nitrogen concentrations increase substantially due to sewage disposal, urban runoff, or industrial waste disposal, eutrophication problems may arise. For example, Hillsborough Bay (Fig. 1), receiving phosphorus from the Alafai River and sewage from Tampa, has high phosphorus and high nitrogen; it experiences eutrophication characterized by frequent phytoplankton blooms and low dissolved oxygen in bottom waters where large amounts of organic material are respired (Federal Water Pollution Control Administration, 1969).

As a first step in understanding effects of phosphorus deposition, the pathways (J_9, J_{11}, and J_{13} of Fig. 9) were increased by a factor of ten. The results are presented in Figs. 17 and 18. Total phosphorus and phosphorus concentrations decreased sharply in waters with an increase in phosphorus in sediments. The new minimum value for the river mouth was 0.4 and the maximum was 1.0 g/m^3 (1.13 and 1.39 previously). For the northern sector of the harbor, the new value ranged from 0.037 to 0.097 g/m^3 (0.45 to 0.75 previously). In the southern sector, the new range was 0.023 to 0.025 g/m^3 (0.3 to 0.41 previously).

Figure 17. Simulation variation of the model in Fig. 9 in which the factors causing phosphorus precipitation (J_9, J_{11}, and J_{13}) were increased by a factor of ten, pumping phosphorus from the water to the sediment.

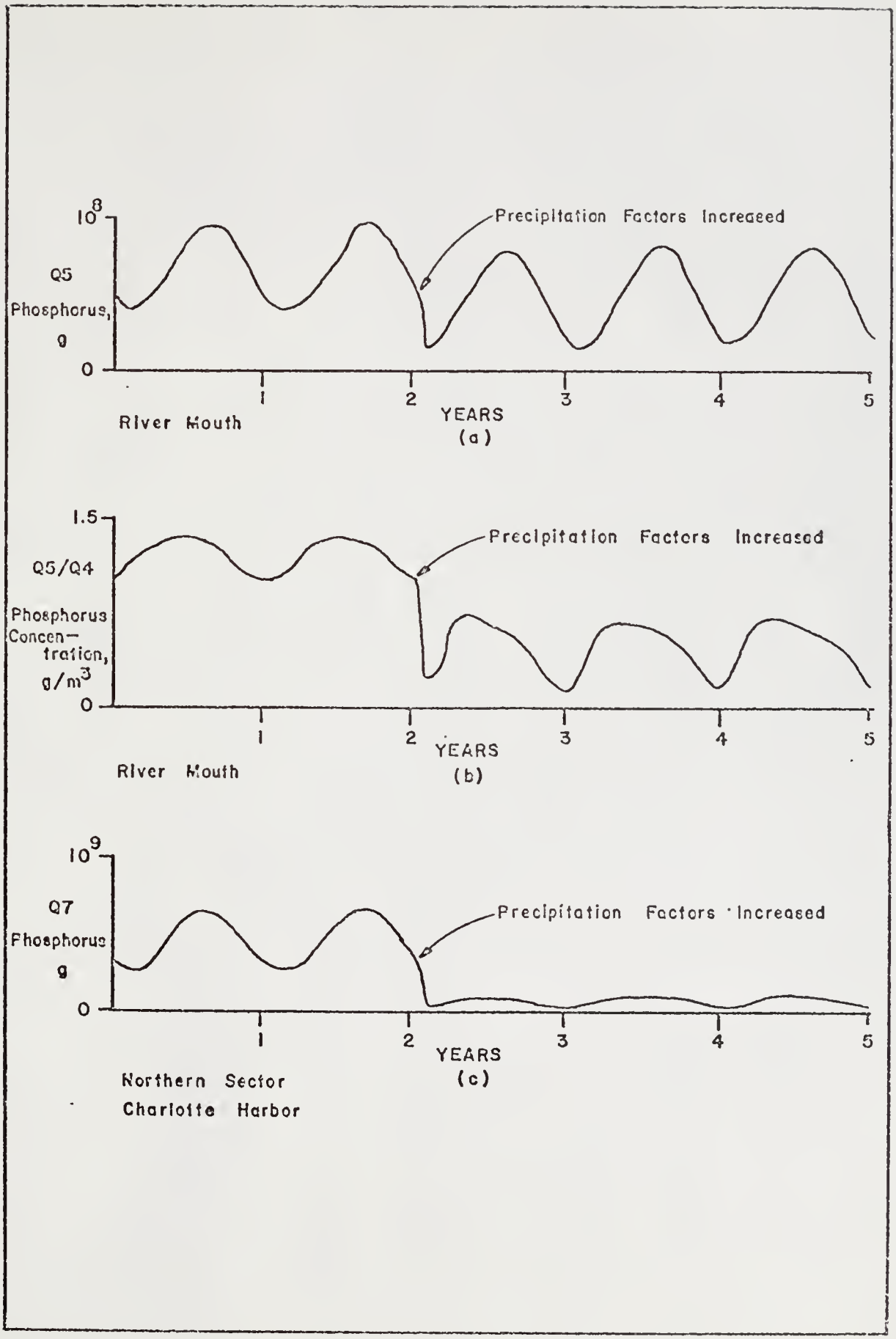
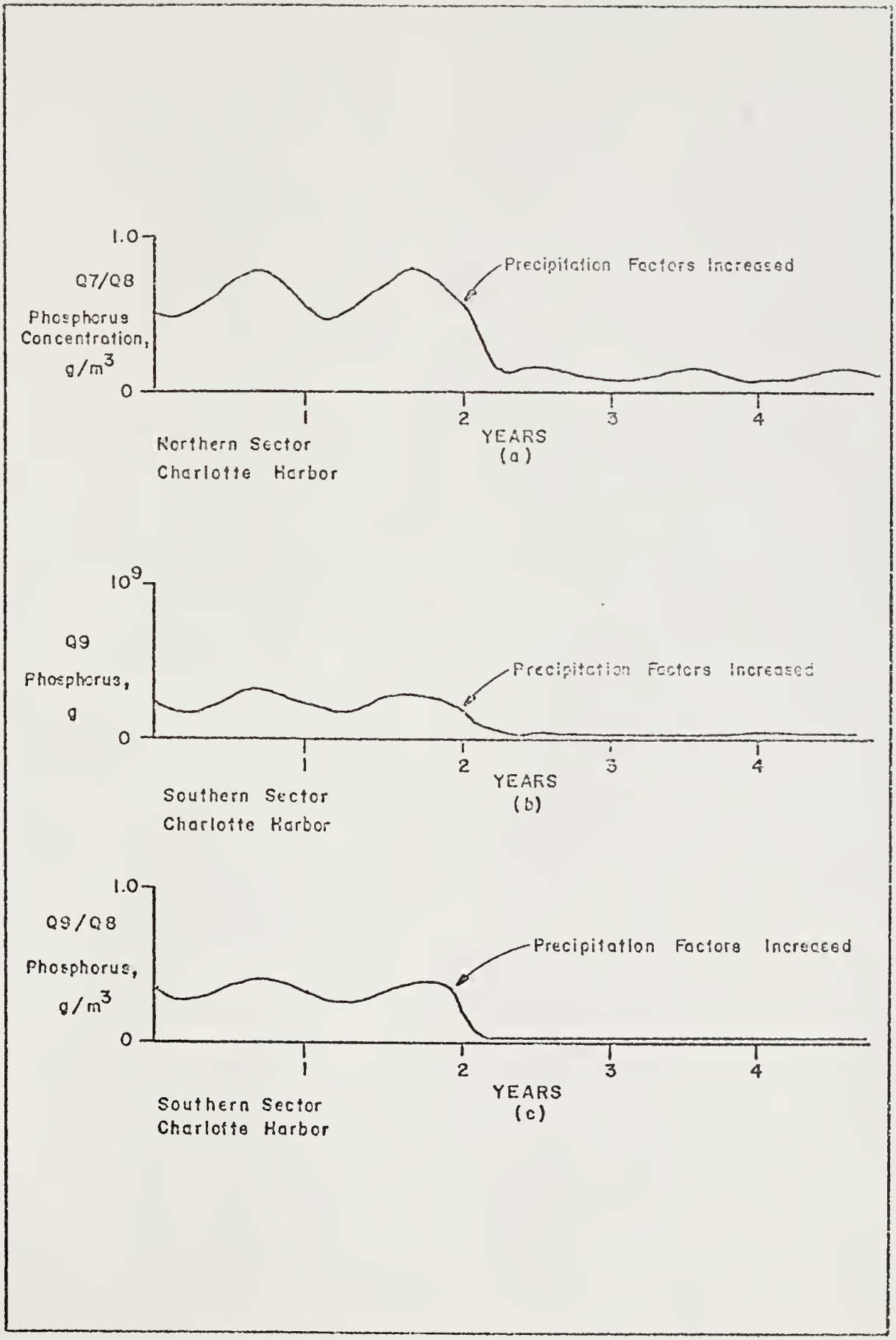

10^8
Q5
Phosphorus, g
0
Precipitation Factors Increased
1
2
3
4
5
YEARS
River Mouth
(a)
1.5
Q5/Q4
Phosphorus Concentration, g/m^3
0
Precipitation Factors Increased
1
2
3
4
5
YEARS
River Mouth
(b)
10^9
Q7
Phosphorus g
0
Precipitation Factors Increased
1
2
3
4
5
YEARS
Northern Sector
Charlotte Harbor
(c)

Figure 18. Simulation variation of the model in Fig. 9 in which the factors causing phosphorus precipitation (J_9, J_{11}, and J_{13}) were increased by a factor of ten, pumping phosphorus from the water to the sediment.

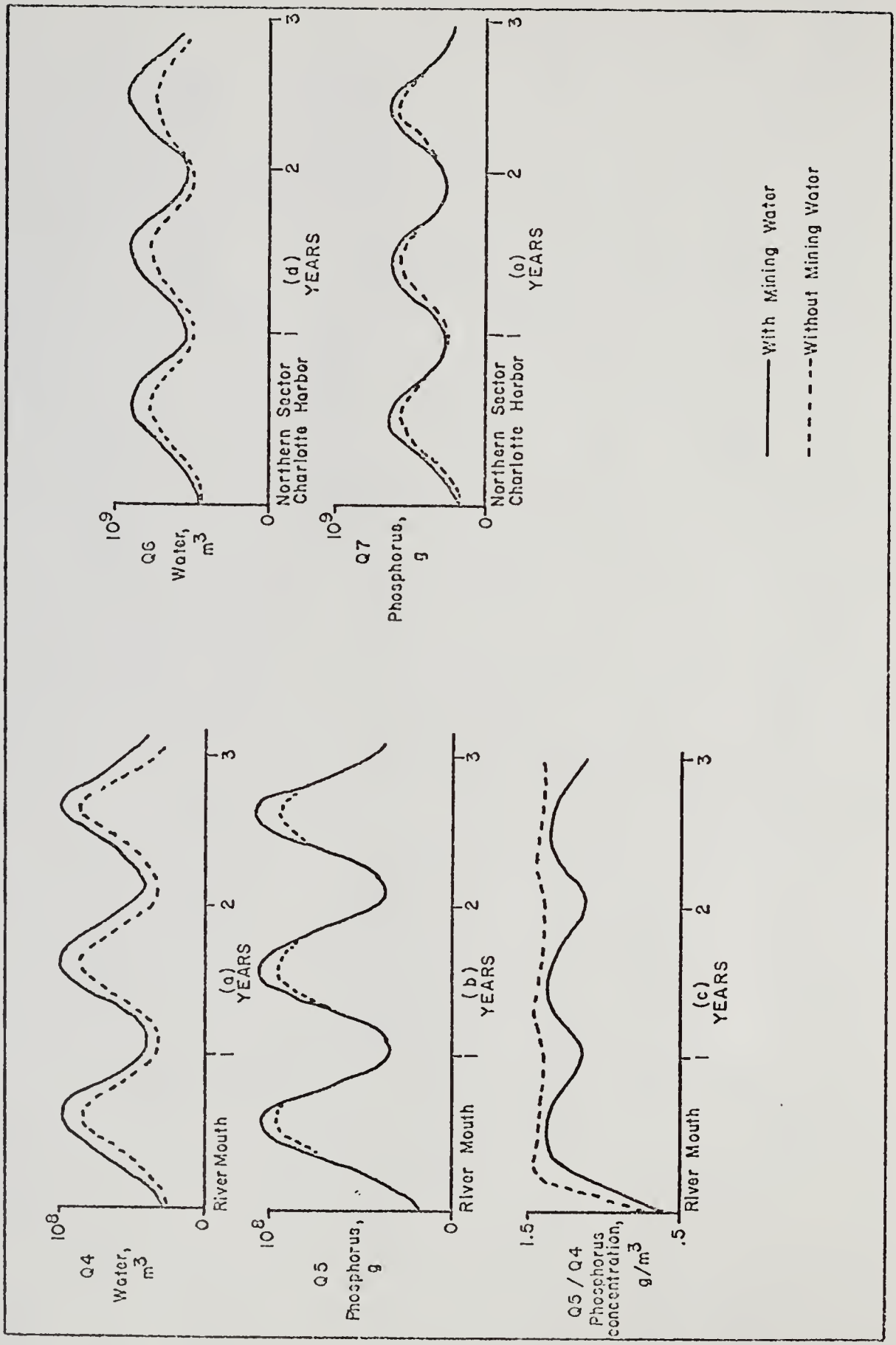

1.0
Q7/Q8
Phosphorus Concentration, g/m3
0
Precipitation Factors Increased
1
2
3
4
YEARS
(a)
Northern Sector
Charlotte Harbor
10^9
Q9
Phosphorus, g
0
Precipitation Factors Increased
1
2
3
4
YEARS
(b)
Southern Sector
Charlotte Harbor
1.0
Q9/Q8
Phosphorus, g/m3
0
Precipitation Factors Increased
1
2
3
4
YEARS
(c)
Southern Sector
Charlotte Harbor

In eutrophic lakes and bays, which have pathways returning nutrients to the surface waters, concentrations often remain high. Hillsborough Bay maintains a total phosphorus concentration of 3 to 7 g/m^3 with the highest value at the mouth of the Alafai River (Federal Water Pollution Control Administration, 1969). This estuarine model (Figs. 9 and 10) may not depict the complete dynamics of phosphorus sedimentation and regeneration which develops under eutrophic conditions. For this reason, a more detailed model of phosphorus and nitrogen interaction was developed (Fig. 25) and simulated.

Mining Water Effluent Decreased to Zero

At the present time, part of the clear effluent from the slime ponds in the mining district is not reused but is wasted to the river (Boyle, 1969). The volume of water discharged is 1.3×10^6 m^3 (J_{3A} in the estuarine model, Fig. 9) at a concentration of 1.0 g/m^3 (J_{3D} in the estuarine model, Fig. 9). In order to determine what effect the constant influx of mining water has on the phosphorus concentration of the river mouth and harbor, these two quantities (J_{3A} and J_{3D}) were set equal to zero and the model simulated. The results are presented in Fig. 19. Water volume was lower in the river mouth and northern sector of the harbor (Figs. 19a and d) by 25% and 4% respectively during the dry season and 10% during periods of maximum flow. Total phosphorus was reduced by 11.5% in the river mouth and 6.2% in

Figure 19. Simulation of the model in Fig. 9 showing the effect of withholding mining water from the Peace River.

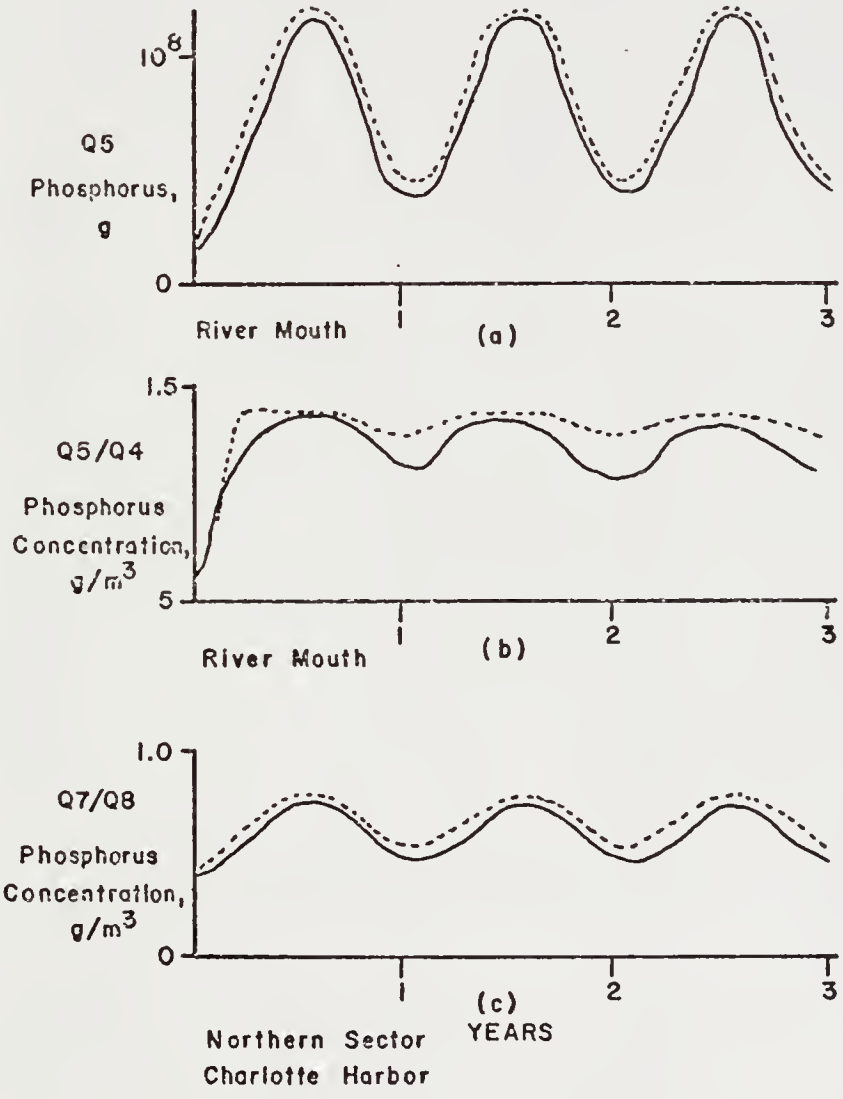

Q4
Water, m3
10^8
0
River Mouth
1
2
3
(a) YEARS
Q5
Phosphorus, g
10^8
0
River Mouth
1
2
3
(b) YEARS
Q5 / Q4
Phosphorus concentration, g/m3
1.5
.5
River Mouth
1
2
3
(c) YEARS
Q6
Water, m3
10^9
0
Northern Sector Charlotte Harbor
1
2
3
(d) YEARS
Q7
Phosphorus, g
10^9
0
Northern Sector Charlotte Harbor
1
2
3
(e) YEARS
With Mining Water
Without Mining Water

the northern sector of the harbor during maximum flow. No reduction was observed during the dry season (Figs. 19b and e). No change in water volume or total phosphorus was observable in the southern sector of the harbor. A concentration change was noticeable in the river mouth (Fig. 19c), but not in either the northern or southern sectors of the harbor. The effect on the river mouth was to negate the concentration minimum which occurred during the dry season (increasing from 1.13 g/m^3 to 1.4 g/m^3 or 24%). Mining water, then, actually diluted the phosphorus concentration of the river slightly. Volume of water was reduced but total phosphorus remained the same, resulting in increased phosphorus concentration. Specht (1950), Lanquist (1953), and Boyle (1969) stated that mining water contributes significantly to the water volume discharged by the Peace River but neither commented on its effect on phosphorus concentrations.

Increase in Sewage Effluent

The twenty million gallons per day (7.54×10^4 m^3/day) of sewage effluent presently being discharged to the Peace River represent a contribution from about 200,000 people. It is assumed that the per capita contribution is 100 gallons of wastewater per day (McGauhey, 1968). In Fig. 20 the effect of a population increase to 500,000 people was studied. Wastewater was increased to 50 million gallons per day (1.89×10^5 m^3/day). The term J_1 in the estuarine

Figure 20. Simulation of the model in Fig. 9 showing the effect of a 2-1/2 times increase in sewage effluent discharged into the Peace River.

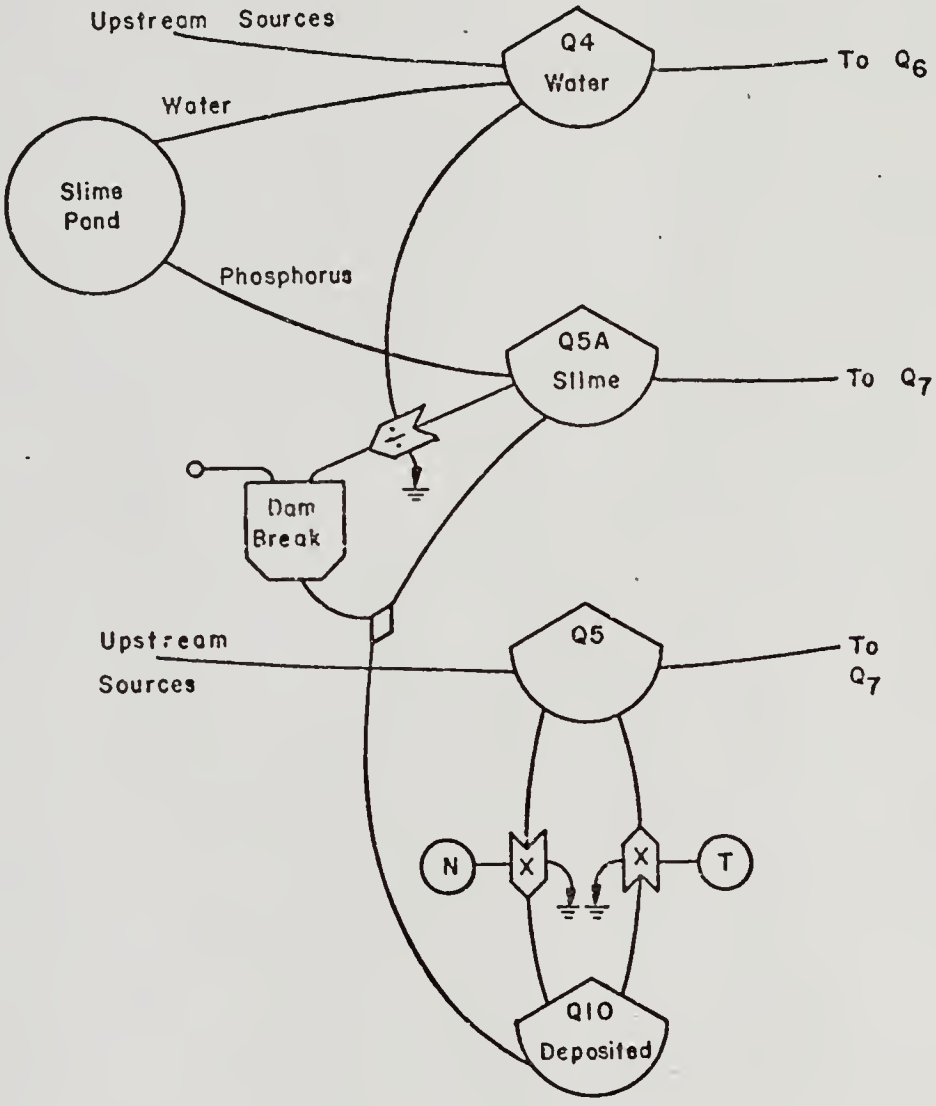

10^8
Q5
Phosphorus, g
0
River Mouth
1
2
3
(a)
1.5
Q5/Q4
Phosphorus Concentration, g/m^3
5
River Mouth
1
2
3
(b)
1.0
Q7/Q8
Phosphorus Concentration, g/m^3
0
1
2
3
(c)
YEARS
Northern Sector
Charlotte Harbor
With Present Sewage Effluent
With High Sewage Effluent

model (Fig. 9) was set equal to 1.89×10^5 m^3/day and the model simulated for three years. Figure 20 shows changes in water volume were too small to be measurable. Total phosphorus increased slightly in the river mouth and northern sector of the harbor (Fig. 20a). The phosphorus concentration curve for the river mouth became flat, showing no dip in the dry season. Whereas concentration during the dry season was 1.13 g/m^3 with the present sewage discharge, it increased to 1.31 g/m^3 with the high sewage discharge (an increase of 16%). No measurable increase was observed during periods of maximum flow.

Dam Break with Slime Spill

Slime spills into the Peace River are readily observable by the white turbid water which can be seen all along the river immediately after the spill. The simulation of a spill gave some insight into long-term effects. The estuarine system model of Fig. 9 was modified slightly for this simulation to separate dissolved and particulate phosphorus compartments in the river mouth. An enormous amount of particulate phosphorus flows into the river during a slime spill and the settling out of the slime into the sediment of the river mouth is proportional to the quantity of slime phosphorus, little affected by relatively lower levels of dissolved phosphorus. The modified model, Fig. 21, includes an additional compartment (Q_{5A}) for slime phosphorus.

Figure 21. Expanded portion of the large model (Fig. 9) required for the slime spill simulation. The storage function, Q_{5A}, for slime phosphorus is added.


Upstream Sources
Q4
Water
To Q_6
Water
Slime
Pond
Phosphorus
Q5A
Slime
To Q_7
Dam
Break
Upstream
Sources
Q5
To
Q_7
N
X
X
T
Q10
Deposited

In the simulation the spill occurred at initial conditions corresponding to the end of two years of simulation of the main program. Results are presented graphically in Figs. 22 and 23. Total phosphorus (including slime) increased drastically to a high of 79.6×10^7 grams and then dropped quickly to 9.0×10^7 grams as the slime settled out to the sediment. A new steady state was then reached with total phosphorus remaining at a higher level than before the spill occurred. The range before the spill was between 4.0×10^7 grams and 13×10^7 grams. After the spill it was between 7.5×10^7 grams and 14.2×10^7 grams. This represents an increase of 87.5% at low flow and 9% at maximum flow.

Phosphorus concentrations in the river mouth showed similar behavior with an initial increase to 18.0 g/m^3 and then a drop to 1.6 g/m^3 as the slime settled out (Fig. 22c). The new steady state rate was higher and the shape of the curve changed. The maximum concentration in the river mouth was during the dry season instead of during periods of maximum flow. The dry season concentration before the spill was 1.13 g/m^3; after the spill it was 1.95 g/m^3, an increase of 72.5%. During periods of maximum flow the concentration before the spill was 1.47 g/m^3; after the spill it was 1.53 g/m^3, an increase of only 4%. Harriss et al. (1972) obtained a four-fold increase in phosphorus in the river mouth after a slime spill (Fig. 24) with a high value of 1.6 g/m^3. The fact that concentration now peaked during

Figure 22. Simulation of Fig. 9 with the additions in Fig. 21 showing the effect of a slime spill.

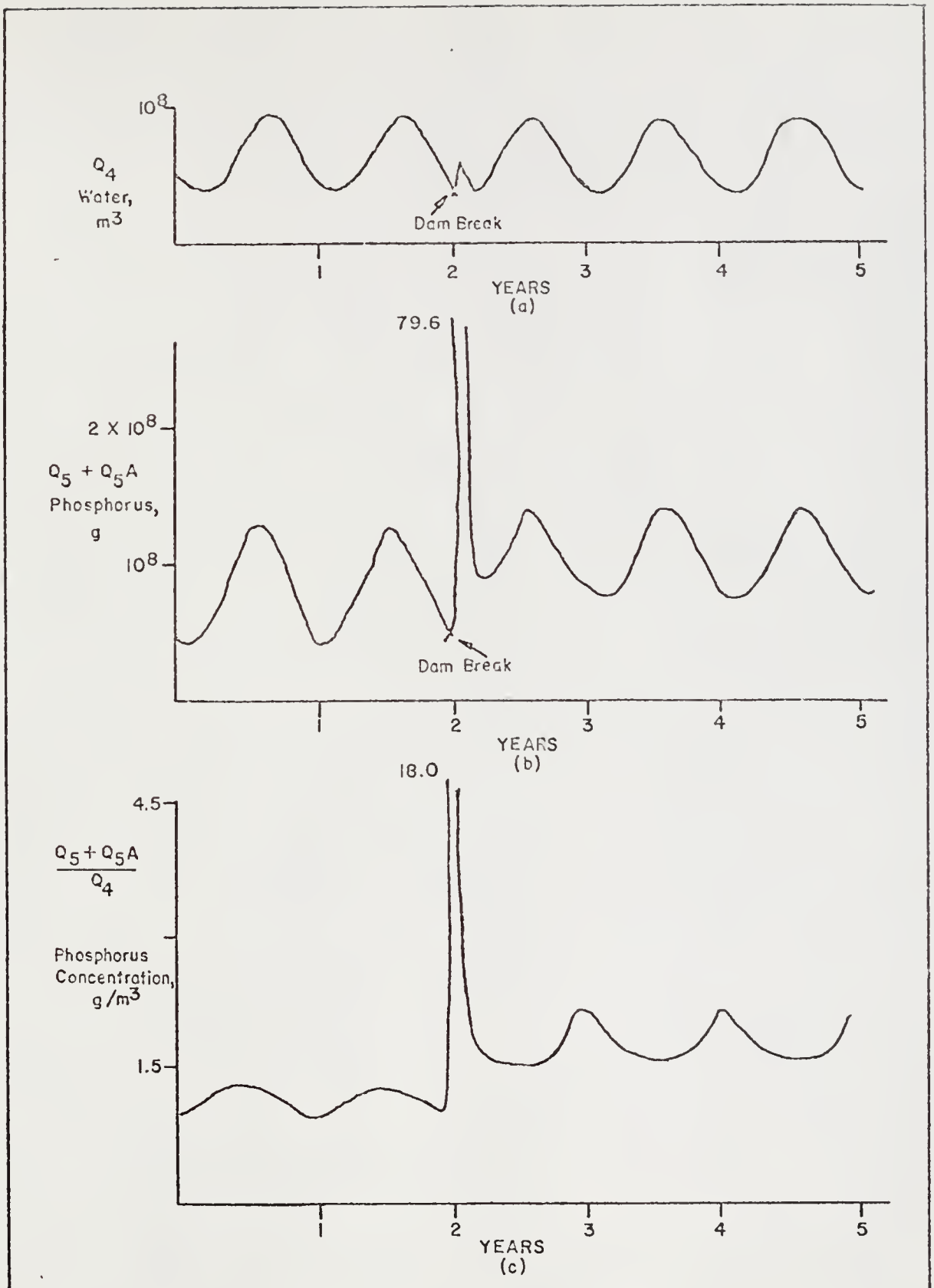

10^8
Q_4
Water,
m^3
Dam Break
1
2
3
4
5
YEARS
(a)
79.6
2×10^8
$Q_5 + Q_5A$
Phosphorus,
g
10^8
Dam Break
1
2
3
4
5
YEARS
(b)
18.0
4.5
$\frac{Q_5 + Q_5A}{Q_4}$
Phosphorus
Concentration,
g/m^3
1.5
1
2
3
4
5
YEARS
(c)
RIVER MOUTH

Figure 23. Simulation of Fig. 9 with the additions in Fig. 21 showing the effect of a slime spill.

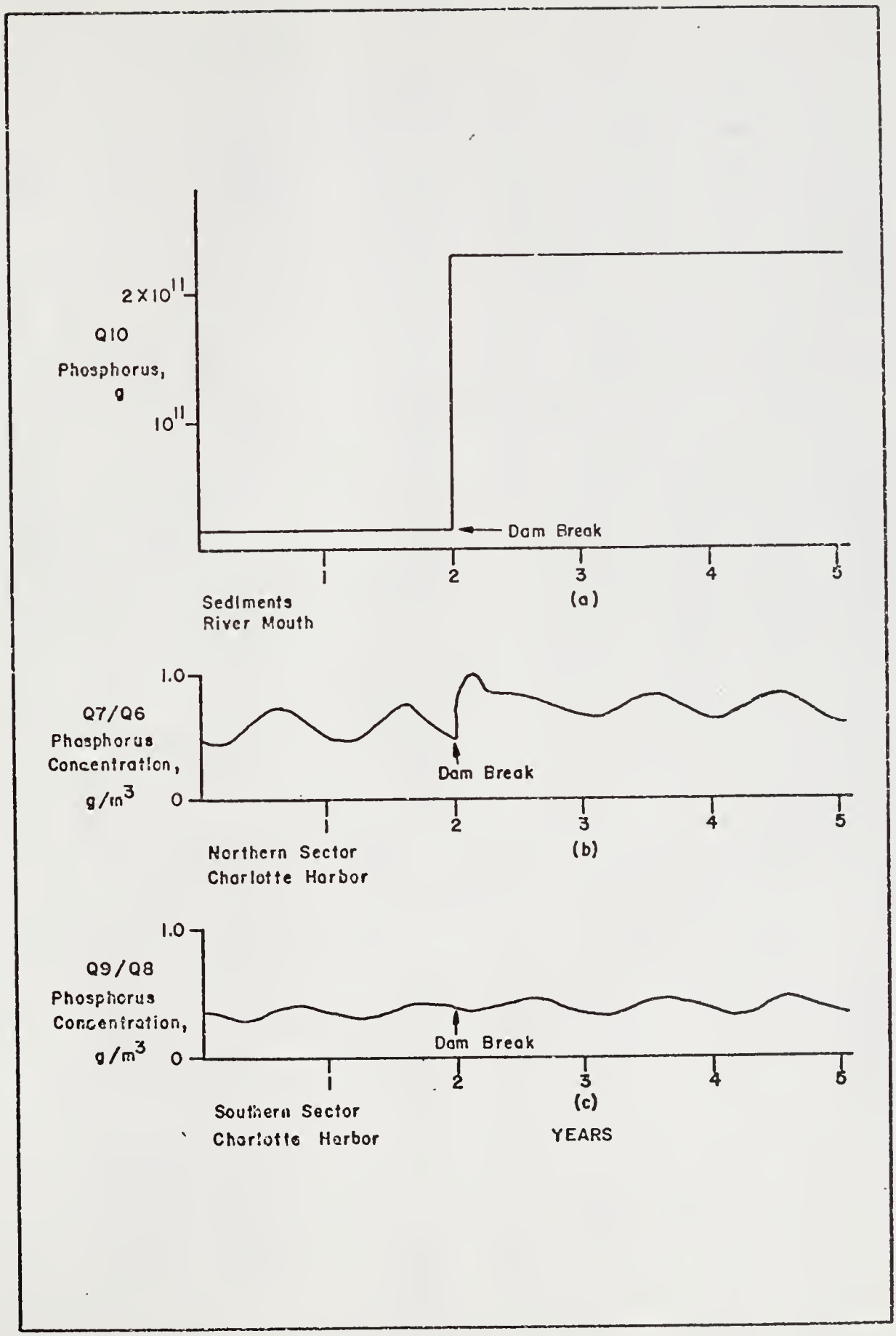
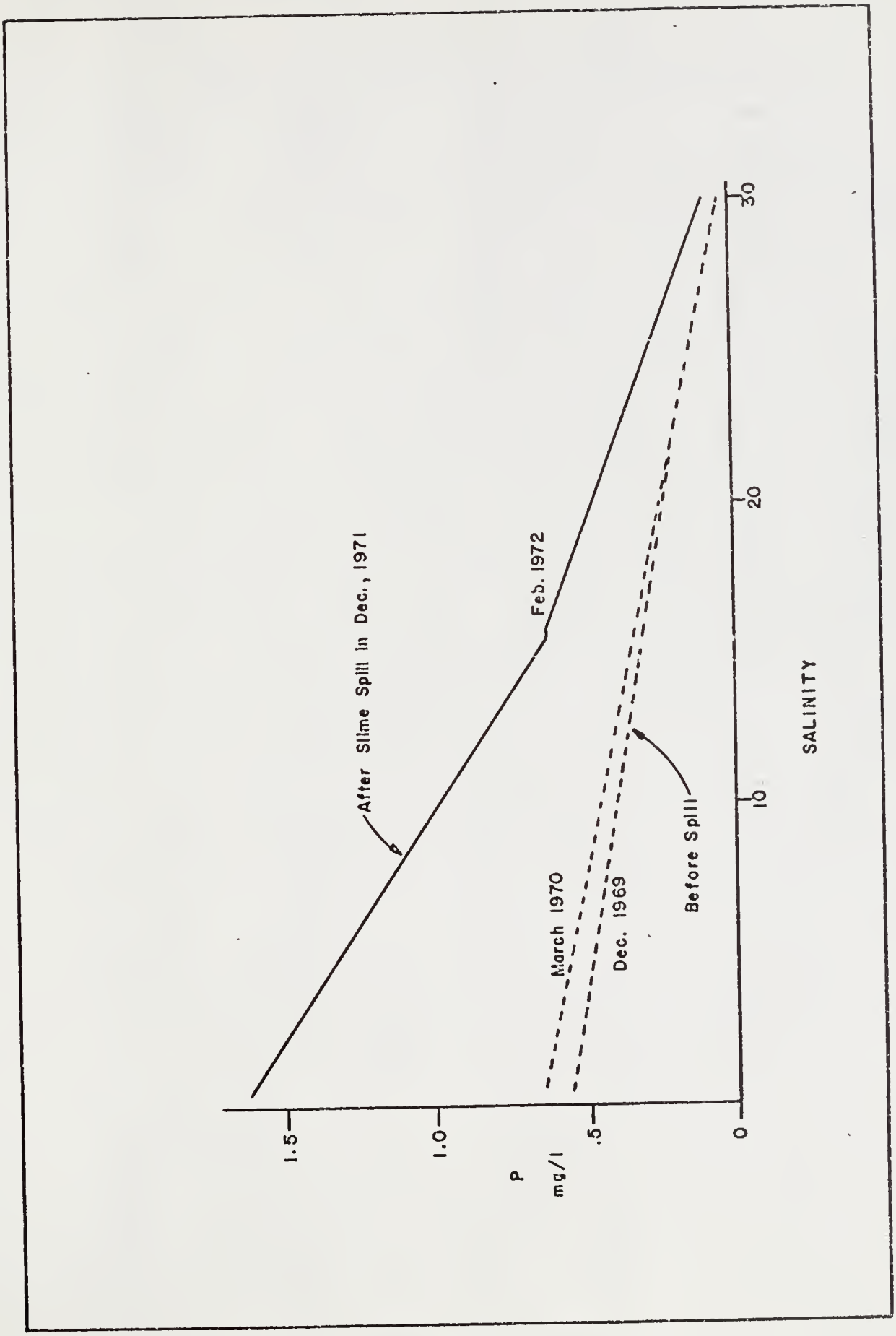

2X10^11
Q10
Phosphorus,
g
10^11
Dam Break
1
2
3
4
5
Sediments
River Mouth
(a)
1.0
Q7/Q6
Phosphorus
Concentration,
g/m^3
0
Dam Break
1
2
3
4
5
Northern Sector
Charlotte Harbor
(b)
1.0
Q9/Q8
Phosphorus
Concentration,
g/m^3
0
Dam Break
1
2
3
4
5
Southern Sector
Charlotte Harbor
(c)
YEARS

Figure 24. Graphical representation of soluble reactive phosphorus versus salinity in the Charlotte Harbor estuarine system before and after a slime spill (from Harriss et al., 1972).


After Slime Spill in Dec., 1971
Feb. 1972
March 1970
Dec. 1969
Before Spill
1.5
1.0
.5
0
P
mg/l
0
10
20
30
SALINITY

the dry season indicated that flux of phosphorus from sediment to surface waters during the dry season was a much larger fraction of the total flux of phosphorus to surface waters than the same flux during periods of maximum river flow.

Most of the slime after a dam break settled into the sediment in the area defined previously as Q_4, which represents the portion of the Peace River that is both sluggish (the river becomes braided) and the portion affected by flood tides. Harriss et al. (1972) stated that the slime settled into the sediment in this portion of the river because of rapid reduction in river current velocity and due to flocculation of the fine-grained phosphate waste by the intrusion of brackish water.

The simulation suggested that turbulence could bring phosphate from the sediment into the surface waters for many years after a slime spill. For the December, 1971, slime spill, Harriss et al. (1972) found that the phosphate slime was reactive with 375 ppm as soluble phosphorus so that the slime in the sediment continues to contribute to the surface water phosphorus concentrations for many years and is eventually flushed into Charlotte Harbor and finally the Gulf of Mexico. Elevated levels were expected for many years. As Harriss et al. (1972) pointed out, the graph of phosphorus versus salinity (Fig. 24) indicated ideal dilution behavior for soluble phosphorus before a slime spill,

but after the spill, due to additions to the water column from the sediment, the less saline samples (river mouth samples) contained more phosphorus than expected from simple dilution.

Figure 23a depicts the change in phosphorus in the river mouth sediments from 1.6×10^{10} grams to 23.2×10^{10} grams. This was an increase of 21.6×10^{10} grams over an area of 1.78×10^{7} m^2 or an increase of 1.21×10^{4} g/m^2. Harriss et al. (1972) indicated that an average of 3 inches of slime was deposited in the December, 1971, spill over an area which represented 65% of the area included in Q_4. Assuming the phosphorus content of the slime was 30% (Harriss et al., 1972), the total contribution to sediment in the December, 1971, spill was 3.24×10^{4} g/m^2, a value which agrees well with that predicted by the simulation.

Figures 23b and c show changes in the phosphorus concentration of Charlotte Harbor after a slime spill. In the northern sector of the harbor at the time of the spill, phosphorus concentration jumped to 1.1 g/m^3 then dropped quickly to 0.85 g/m^3; after the slime spill it was 0.6 g/m^3, an increase of 33%. During maximum flow periods the concentration was 0.75 g/m^3; after the slime spill it was 0.85 g/m^3 (an increase of 13%). The dry season increase was more severe due to the peak in concentration in the upriver compartment.

Little change was observed due to the slime spill in the southern sector of the harbor (Fig. 23c).

Nitrogen, Phosphorus, and Productivity in the Peace River Mouth

Phytoplankton populations in Charlotte Harbor were smaller than populations measured in other Florida estuaries (Harriss et al., 1972, and Spence, 1971). There may be larger populations of algae on the bottom. Since both phosphorus and nitrogen are critical nutrients for algal growth, and since high values of phosphate are present in the river mouth and harbor, there is a possibility that the low nitrogen concentrations are limiting the phytoplankton populations. Ryther and Dustan (1971) demonstrated that insufficient supplies of dissolved nitrogen limit algal growth in the coastal marine waters off Long Island.

A model depicting some interactions of phosphorus, nitrogen, light, and turbidity in the Peace River Estuary is shown in Fig. 25. Table 5 gives the numerical values with accompanying notes found in Appendix A describing in detail the derivation of each number.

The model simulated is a simplification of the more comprehensive system shown in Fig. 26. The simulated version does not include recycle pathways. This is believed acceptable for the following reasons: the organic load of the river is not large (averaging 50 ppm, personal communication with Dequine); dissolved oxygen is high (9.2 to 12.5 mg/l in surface waters and 4.0 to 11.3 mg/l in bottom waters, Dequine); and the estuary is a flowing water one,with the water exchanged every 3.5 days (Table 4). A test simulation

Figure 25. Model of nitrogen and phosphorus interaction with production in the Peace River estuary. This model shows the details within Q_5 of the large overall system (Figs. 9 and 10). Shown on the diagram are the mathematical terms and numerical values associated with each state variable and pathway. Also included are the differential equations written directly from the diagram. Units for the light flows are Kcal/day; all other flows are 10^6 g/day.

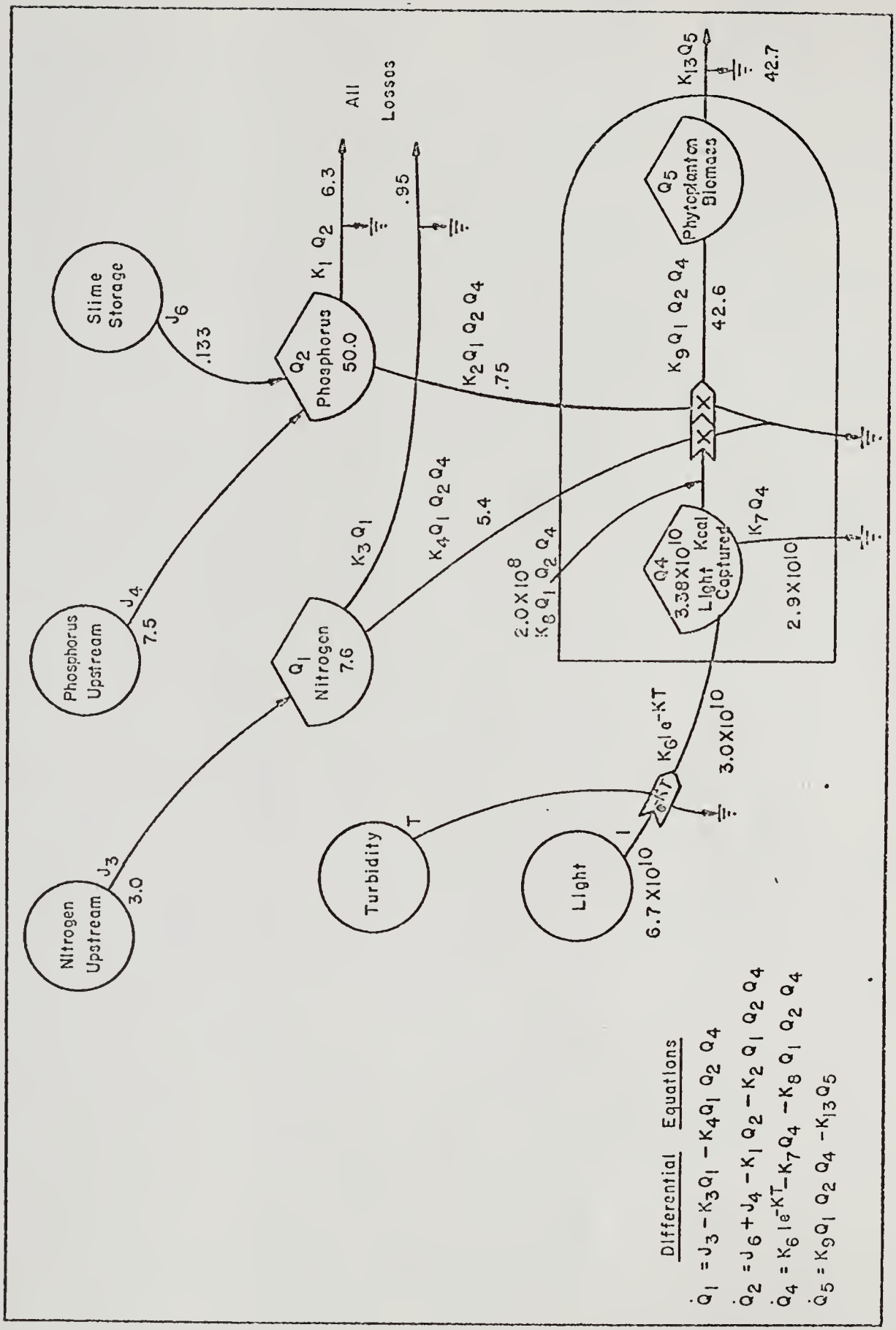

Nitrogen Upstream
J3
3.0
Phosphorus Upstream
J4
7.5
Slime Storage
J6
.133
Turbidity
T
Light
I
6.7 X 10^10
Q1 Nitrogen 7.6
Q2 Phosphorus 50.0
Q4 3.38X10^10 Light Kcal Captured
Q5 Phytoplankton Biomass
K1 Q2
6.3
All Losses
.95
K2 Q1 Q2 Q4
.75
K3 Q1
K4 Q1 Q2 Q4
5.4
2.0X10^8
K8 Q1 Q2 Q4
K9 Q1 Q2 Q4
42.6
K7 Q4
2.9X10^10
K13 Q5
42.7
K6 I e^-KT
3.0X10^10
Differential Equations
Q̇1 = J3 - K3Q1 - K4Q1 Q2 Q4
Q̇2 = J6 + J4 - K1 Q2 - K2 Q1 Q2 Q4
Q̇4 = K6 Ie^-KT - K7Q4 - K8 Q1 Q2 Q4
Q̇5 = K9Q1 Q2 Q4 - K13Q5

Table 5

Sources, Storages, and Rates for the
Phosphorus-Nitrogen Interaction Model (Fig. 25)

Mathematical Term	Note (Appendix A)	Quantity	Numerical Value	Source
Q_1	1	Nitrogen stored	7.5×10^6 g	Finucane and Dragovich (1959) Connell and Associates (1972)
Q_2	2	Phosphorus stored	50.0×10^6 g	Alberts *et al.* (1970)
Q_4	3	Light captured	3.38×10^{10} kcal	E. P. Odum (1971) H. T. Odum (1971)
Q_5	4	Phytoplankton stock	42.7×10^6 g	Spence (1971)
I	5	Sun	6.76×10^{10} kcal	E. P. Odum (1971)
J_2	6	Turbidity	10 ppm	Lanquist (1953)
J_3	7	Nitrogen from upstream	3.0×10^6 g/day	U.S. Geol. Surv. (1961-1968) Odum *et al.* (1955)
J_4	8	Phosphorus from upstream	7.5×10^6 g/day	Previous simulation (Fig. 9)
J_6	9	Phosphorus in sediment to phosphorus in surface waters	0.133×10^6 g/day	Previous simulation (Fig. 9)

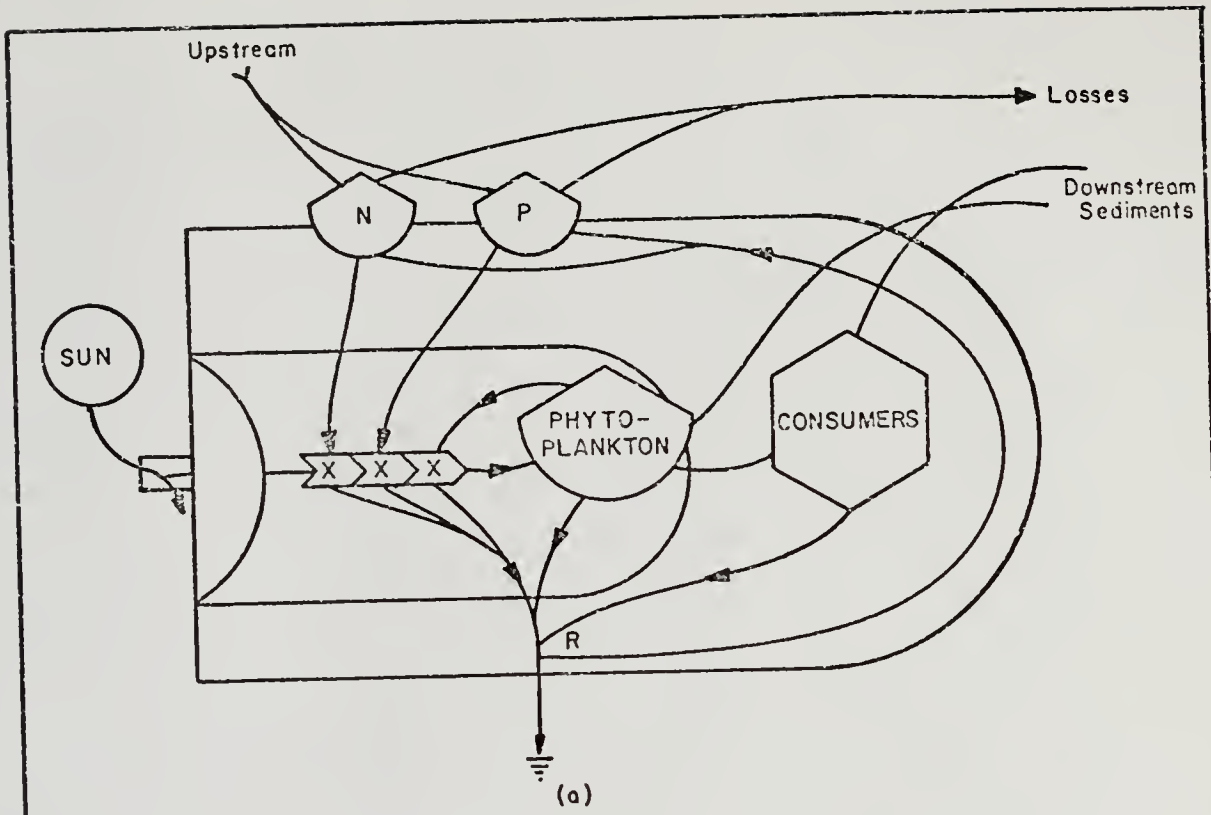
Table 5 (continued)

Mathematical Term	Note (Appendix A)	Quantity	Numerical Value	Source
K_1Q_2	10	Phosphorus exported downstream and to sediments	6.3×10^6 g/day	Previous simulation (Fig. 9)
$K_2Q_1Q_2Q_4$	11	Phosphorus incorporated into phytoplankton biomass	0.75×10^6 g/day	Sverdrup (1942)
K_3Q_1	12	Nitrogen exported downstream	0.95×10^6 g/day	Harriss et al. (1972) Finucane and Dragovich (1959)
$K_4Q_1Q_2Q_4$	13	Nitrogen incorporated into phytoplankton biomass	5.4×10^6 g/day	Sverdrup (1942)
K_6Ie^{-KT}	14	Sun into light storage	3.0×10^{10} kcal/day	E. P. Odum (1971)
K_7Q_4	15	Light dispersed	2.9×10^{10} kcal/day	E. P. Odum (1971)
$K_8Q_1Q_2Q_4$	16	Light energy incorporated into phytoplankton biomass	1.92×10^8 kcal/day	E. P. Odum (1971)
$K_9Q_1Q_2Q_4$	17	Production	42.7×10^6 g/day	E. P. Odum (1971)
$K_{13}Q_5$	18	Exports from phytoplankton	42.7×10^6 g/day	Steady state calculation

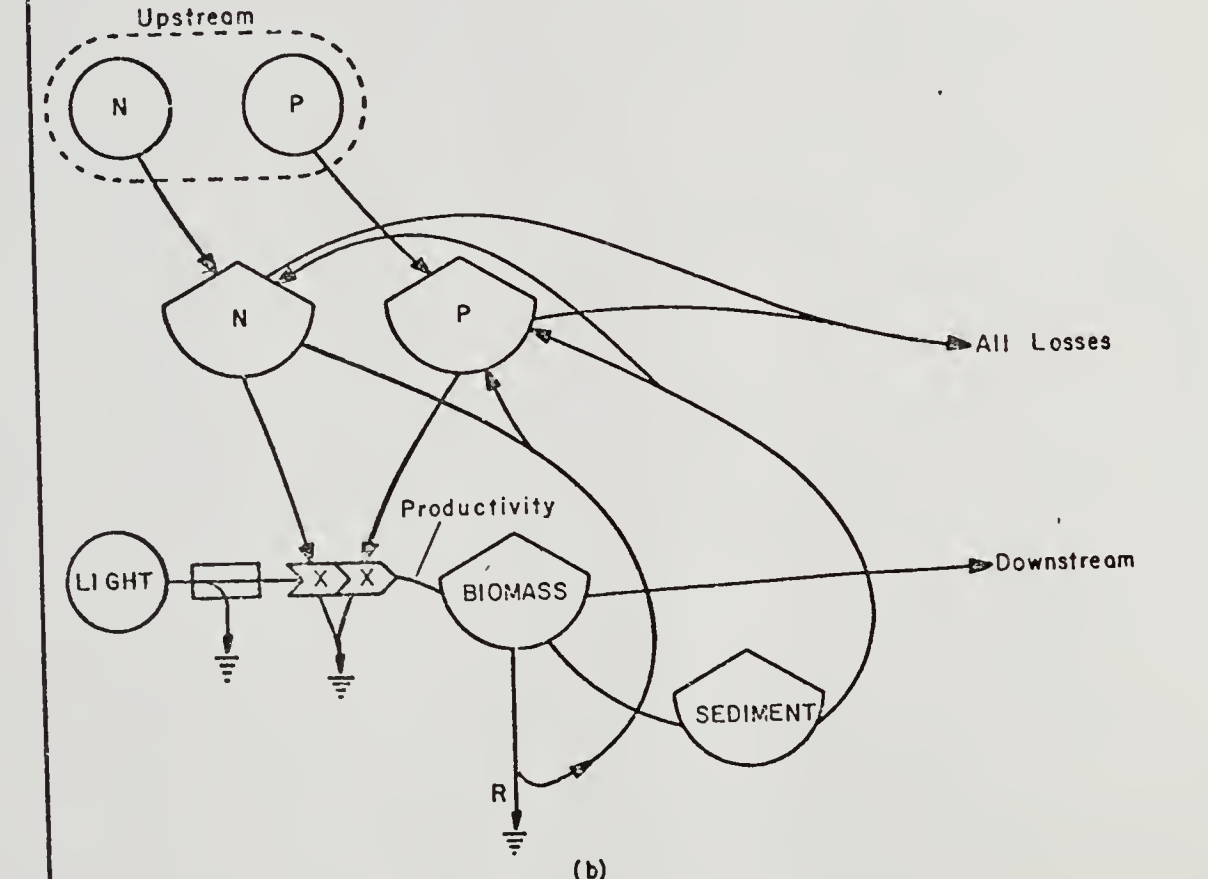
Figure 26. a. Ecosystem representation showing producers, consumers, and nutrient recycle pathways.

b. Model simulated in order to test the behavior for simulation of the simplified model (Fig. 25).

is Michaelis-Menton module which delivers an output KS/K+S.


Upstream
Losses
Downstream
Sediments
N
P
SUN
X
X
X
PHYTO-
PLANKTON
CONSUMERS
R

(a)


Upstream
N
P
N
P
All Losses
Productivity
LIGHT
X
X
BIOMASS
Downstream
SEDIMENT
R

(b)

of Fig. 26b indicated similar behavior for the model in Fig. 25 and Fig. 26b (see results in Fig. 27).

Data Evaluation

A turbidity value of 10 ppm is taken as a typical level for the estuary (Lanquist, 1953); however, values as high as 900 ppm were recorded in the area after slime spills. Spence (1971) studied diatoms in Charlotte Harbor, stating that diatoms, particularly Cyclotella species, dominated the phytoplankton. She finds an average cell count for diatoms of 5.34×10^5 cells/liter with a range of 0.2×10^5 to 9.5×10^5 cells/liter. This converts to an average diatom concentration of 0.3 g/m^3, or a total phytoplankton weight for the area of 15×10^6 g. The model (Fig. 25) shows a standing crop of 42.7×10^6 g. Since Spence's value is for diatoms only and the diatom species are small phytoplankton, the starting value of 42.7×10^6 g, corresponding to 0.85 g/m^3, is acceptable.

Connell and Associates (1972), in an Environmental Assessment Study of the Punta Gorda area, found an average pennate diatom population of 3×10^5/liter with a high value of 8×10^5 liter. The volumes of different species of diatoms can vary enormously from 2×10^{-2} mm^3 to 2×10^{-8} mm^3 (Harvey, 1950) or, assuming the diatoms have a similar density to water and taking the average population value of 3×10^5/liter, this value range corresponds to a concentration range of 6,000 g/m^3 to 6×10^{-3} g/m^3, a range of six orders of magnitude with an average of 6 g/m^3. The pennate diatoms

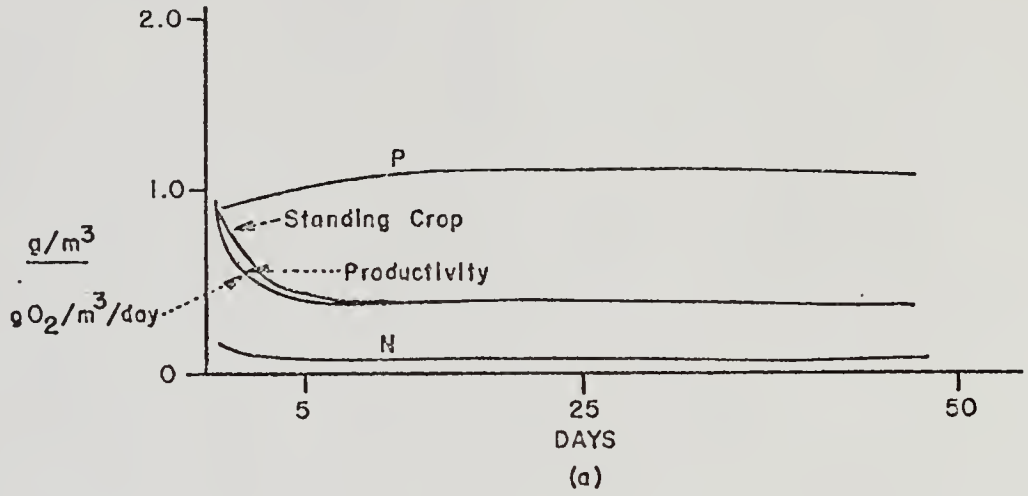
referred to by Connell and Associates are relatively small so that the original standing crop estimate of 0.85 g/m^3 was used.

Simulation Evaluation

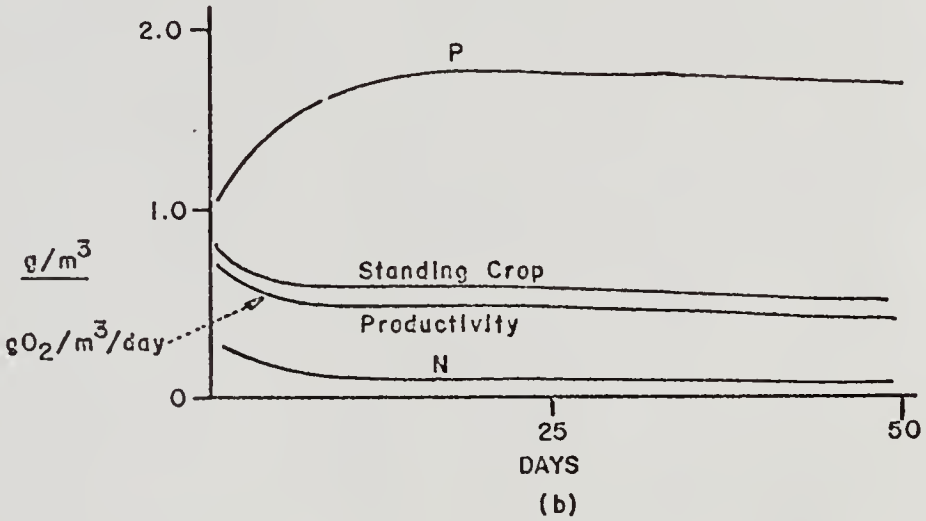
Figure 27a depicts the results of the simulation of the model using the numbers for state variables and pathways given on the system diagram (Fig. 25) and in Table 5. For comparison, Fig. 27b shows the results of simulation of the model in Fig. 26b. The results are similar. Phosphorus concentration increased from 1.0 g/m^3 at the start to 1.17 g/m^3 at steady state and total dissolved nitrogen concentration decreased from 0.15 g/m^3 at the initial condition to 0.058 g/m^3 at steady state. Connell and Associates stated that dissolved total nitrogen concentrations were usually less than 0.1 ppm. Light remained constant and phytoplankton standing crop decreased from 0.8 g/m^3 to 0.43 g/m^3, while productivity decreased from 1.0 g/m^3/day to 0.42 g/m^3/day at steady state. The indication was that the steady state condition reached in five days depleted total nitrogen even more than the low starting value, while standing crop and net productivity also decreased to low steady state values. The steady state generated by the simulation then yielded a standing crop of 0.43 g/m^3 and a production of 0.42 g/m^3/day, which is low. Nitrogen in the water was pulled almost to zero (0.058 g/m^3), indicating the role of high phosphorus in causing nitrogen to limit productivity.

Figure 27. a. Simulation results of the model shown in Fig. 25.

b. Simulation results of the model shown in Fig. 26b.


2.0
1.0
0
g/m3
gO2/m3/day
P
Standing Crop
Productivity
N
5
25
50
DAYS

(a)


2.0
1.0
0
g/m3
gO2/m3/day
P
Standing Crop
Productivity
N
25
50
DAYS

(b)

Increased Population

In order to test the system's sensitivity to an increase in available nitrogen, the upstream source (J_3) of nitrogen was increased from its initial condition of 3.0×10^6 g nitrogen input (0.47 g/m^3) successively to 7.0×10^6 g, 10.0×10^6 g and 15.0×10^6 g. Results of this increased nitrogen input are shown in Fig. 28. Note that nitrogen concentration in the surface waters increased successively and phytoplankton standing crop increased. Phosphorus levels were pulled down slightly to a low of 0.95 g/m^3 in Fig. 28c. Light captured remained constant. Graphs of steady state nitrogen concentrations versus phytoplankton standing crop and productivity are given (Fig. 29). Both standing crop and productivity steadily increased as the available nitrogen increased. The nitrogen levels were within the expected range as population pressures increased sewage and urban runoff. Increasing the population from the level of about 200,000 people to 500,000 people and assuming secondary treatment for all sewage would result in a nitrogen input from sewage alone of 7×10^6 g (shown in Fig. 28a). This simulation yielded a nitrogen concentration in the surface waters of 0.142 g/m^3, a standing crop of 0.97 g/m^3, and a net productivity of 0.97 g O_2/m^3/day. A total population of one million people would result in a nitrogen input from sewage alone of 10×10^6 g (shown in Fig. 28b). The simulation yielded a surface water nitrogen concentration

Figure 28. Simulation of the model in Fig. 25 showing changes in stocks and net productivity in the surface water for levels of available nitrogen.

a. Results of nitrogen input (J_3) increase to 7.0×10^6 g/day (input concentration 1.11 g/m^3), yielding a steady state stock of nitrogen of 0.14 g/m^3 (Q_1).

b. Results of nitrogen input (J_3) increase to 10×10^6 g/day (input concentration of 1.6 g/m^3), yielding a steady state stock of nitrogen of 0.21 g/m^3.

c. Results of nitrogen input (J_3) increase to 15×10^6 g/day (input concentration of 2.4 g/m^3), yielding a steady state stock of nitrogen of 0.36 g/m^3.

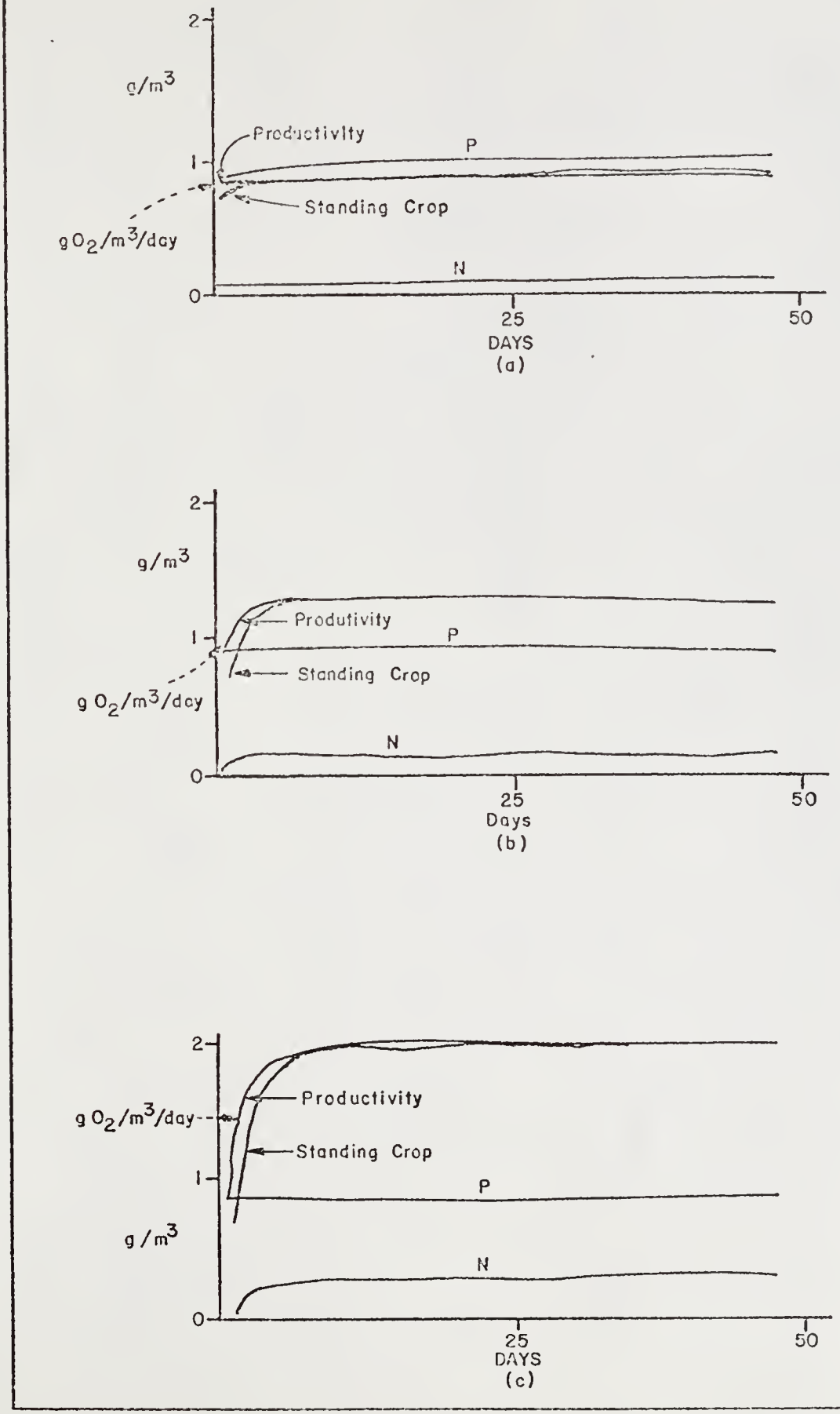
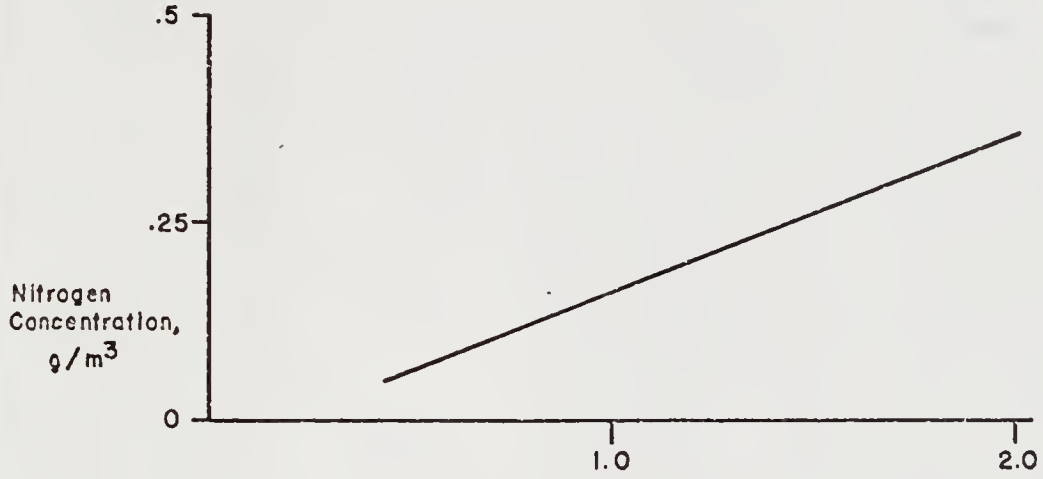
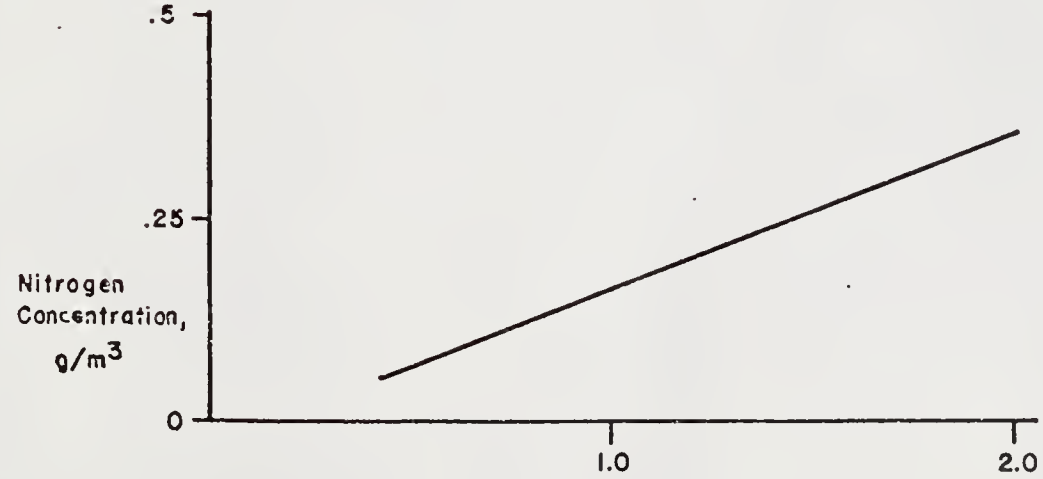

2
g/m3
Productivity
P
1
Standing Crop
g O2/m3/day
N
0
25
50
DAYS
(a)
2
g/m3
Produtivity
P
1
Standing Crop
g O2/m3/day
N
0
25
50
Days
(b)
2
g O2/m3/day
Productivity
Standing Crop
P
1
g/m3
N
0
25
50
DAYS
(c)

Figure 29. Steady state nitrogen concentration versus steady state phytoplankton standing crop (a) and steady state productivity (b).


.5
.25
0
Nitrogen Concentration, g/m3
1.0
2.0
Standing Crop
g/m3

(a)


.5
.25
0
Nitrogen Concentration, g/m3
1.0
2.0
Productivity,
g O2/m3/day

(b)

of 0.21 g/m^3, a standing crop of 1.39 g/m^3 and a productivity of 1.34 g O_2/m^3/day. If nitrogen from runoff from increased urban areas were added, standing crop and productivity might be higher still. Nitrogen from urban runoff is in the range of 0.88 grams per square meter of land use area per year (Brezonik and Shannon, 1971, from Weibel, 1969). Assuming an urban land area the size of Tampa and St. Petersburg, 0.88 g/m^2/year converts to an additional input of $2x10^6$ g N/day. Figure 28c depicts the results of simulation in which the input of nitrogen was $15x10^6$ g/day, a value which could easily be reached from the sum of agriculture inputs, sewage, urban runoff, and natural drainage. Note that (Fig. 28c) the surface water nitrogen concentration, although increasing, still remained relatively low (0.36 g/m^3). Phosphorus was pulled down slightly from an initial steady state value of 1.17 g/m^3 to 0.95 g/m^3. Standing crop increased to 2.0 g/m^3 and productivity was 2.0 g O_2/m^3/day.

Harriss et al. (1972) conducted a nutrient bioassay experiment in the Peace River estuary; they measured the effect of additions of dissolved nitrogen and silica on radiocarbon uptake by the natural phytoplankton communities in Charlotte Harbor. Their results indicated that increased quantities of dissolved nitrogen stimulated phytoplankton growth slightly.

Production values measured in Hillsborough Bay (Federal Water Pollution Control Administration, 1969) gave added perspective to those obtained from this simulation. Total dissolved nitrogen there ranged from 0.1 g/m^3 to 1.0 g/m^3 and the average net photosynthesis measured was 2.54 g O_2/m^3/day. Hillsborough Bay is one of Florida's waste recovery estuaries.

Test for Light and Phosphorus as Limiting Factors

The simulation indicated that levels of productivity are linearly sensitive to nitrogen. Light and then phosphorus were increased and the model again simulated with the results in Fig. 30. Neither increasing the light by lowering turbidity nor increasing phosphorus increased standing crop or productivity. The steady state standing crop under initial conditions was 0.43 g/m^3; it increased to only 0.45 g/m^3 when light and phosphorus were increased.

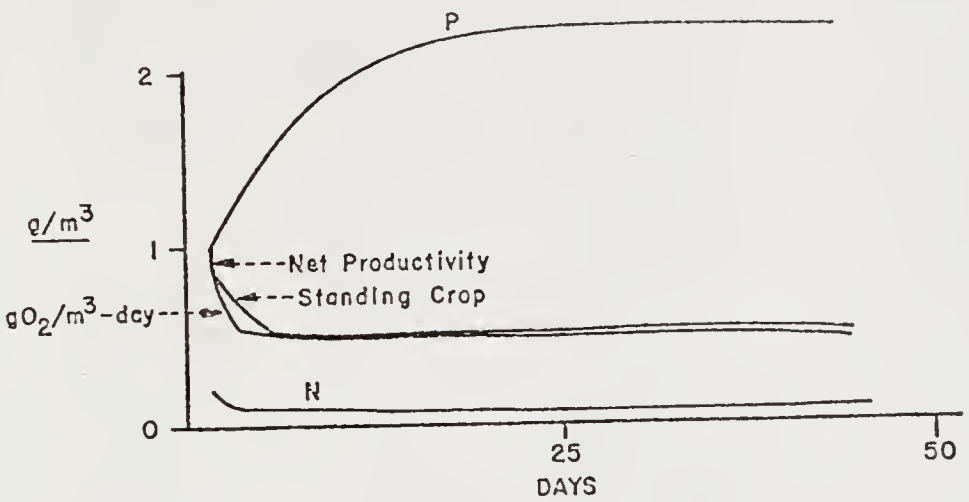
Phosphorus Deposited in Sediment

A variation simulated in the large Peace River-Charlotte Harbor system model (Fig. 9) was the effect of nitrogen levels on phosphorus being deposited in sediment. From the standpoint of eutrophication, nutrient deposition into sediment is important to respiration of organic material exerting a benthic oxygen demand later. The amount of organic material, from which can be derived the amount of phosphorus going into sediment as nitrogen levels increase,

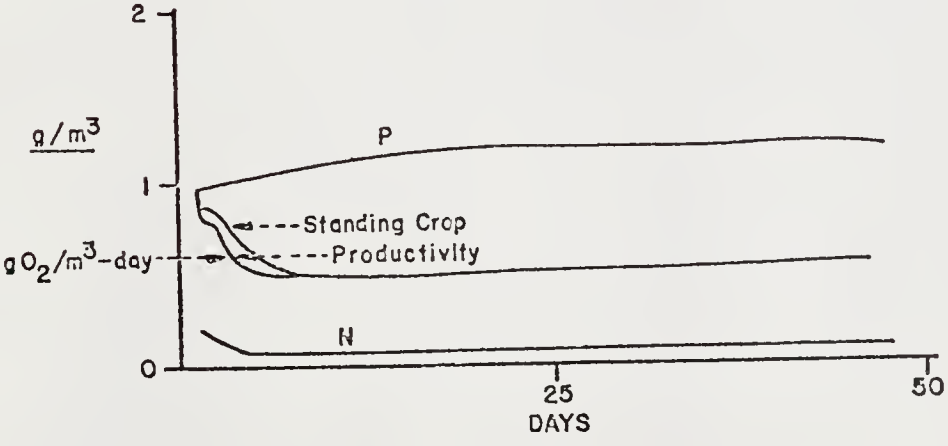
Figure 30. Simulation of the model in Fig. 25 showing stocks and net productivity with time for:

a. an increase in the upstream source of phosphorus (J_4) from 7.6×10^6 g/day (1.2 g/m^3/day) to 15×10^6 g/day (2.3 g/m^3/day) resulting in a stock of phosphorus of 2.3 g/m^3.

b. a decrease in turbidity resulting in increased light.


P
2
g/m3
1
---Net Productivity
---Standing Crop
gO2/m3-day
N
0
25
50
DAYS

(a)


2
g/m3
P
1
---Standing Crop
gO2/m3-day
----Productivity
N
0
25
50
DAYS

(b)

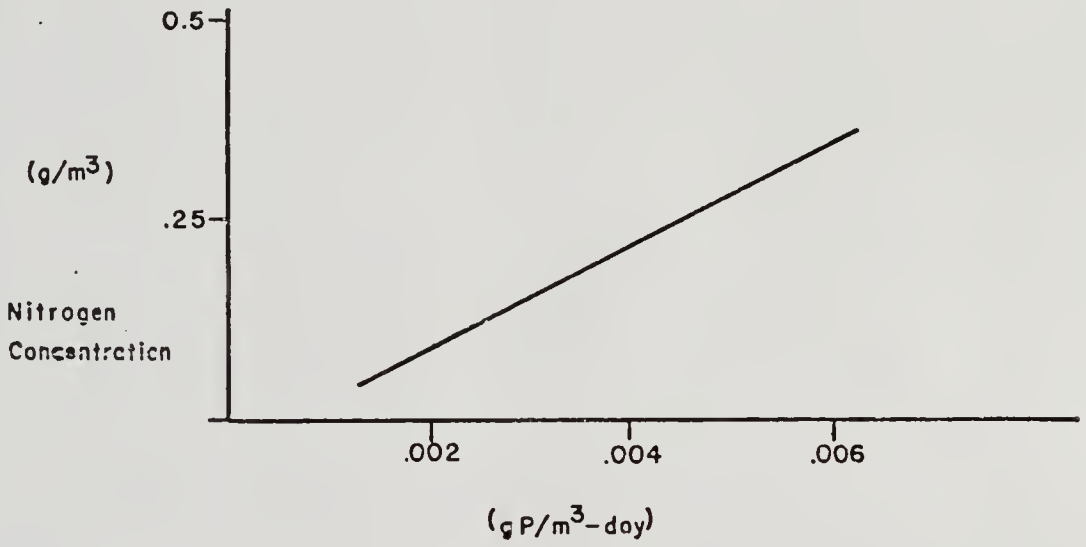
was calculated. The output of the phytoplankton standing crop (Q_5) of Fig. 25 consists of downstream export and export to sediment. Figure 31 is a plot of nitrogen concentration in surface waters as a function of phosphorus into sediment obtained from simulation of the smaller model in Fig. 25. The nitrogen concentration (0.15 g/m^3) assumed in the simulation of the large model (Fig. 9) was subsequently increased by a factor of 10 with the simulation results in Fig. 17 and 18. The increased value of nitrogen increased the influx of phosphorus into sediment to 0.058 g/m^3/day compared to the initial flux of 0.0027 g/m^3/day. Note that these fluxes are similar to those from the simulation of the more detailed model.

Pomeroy et al. (1972) gave values ranging from 8 to 14 mg P/m^2/day as the exchange rates for three shallow turbid estuaries on the Georgia Coast. Assuming an average of 11 mg P/m^2/day yields a flux of 0.0038 g/m^3/day for the Peace River estuary. This is certainly well within the range of that predicted by the simulation for various nitrogen levels (Fig. 31).

Turbidity and Phosphorus Slime

Turbidity values in the form of clay reach extremely high levels (several hundred ppm) following a slime spill upriver. The small model (Fig. 25) was simulated for increased turbidity values with graphical results given in Fig. 32. Since light became the limiting factor to

Figure 31. Nitrogen concentration in the surface water predicted from the simulation of the model in Fig. 25 versus phosphorus deposited in the sediment calculated from simulation results.

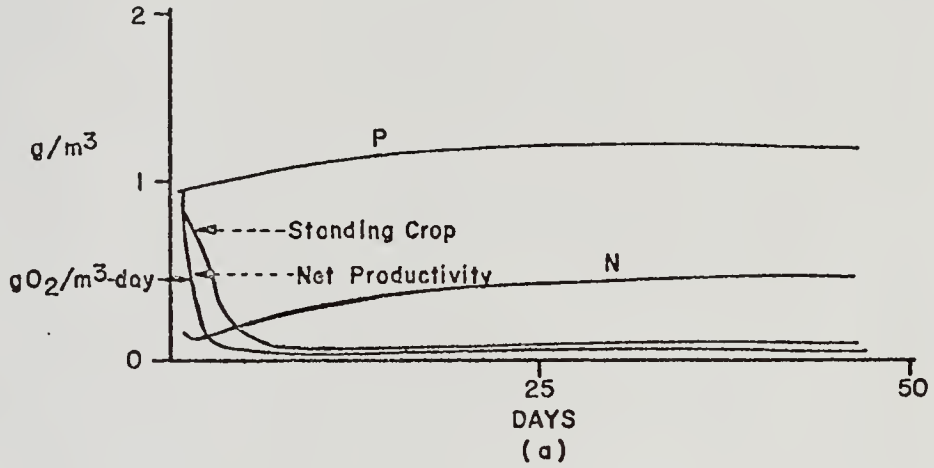


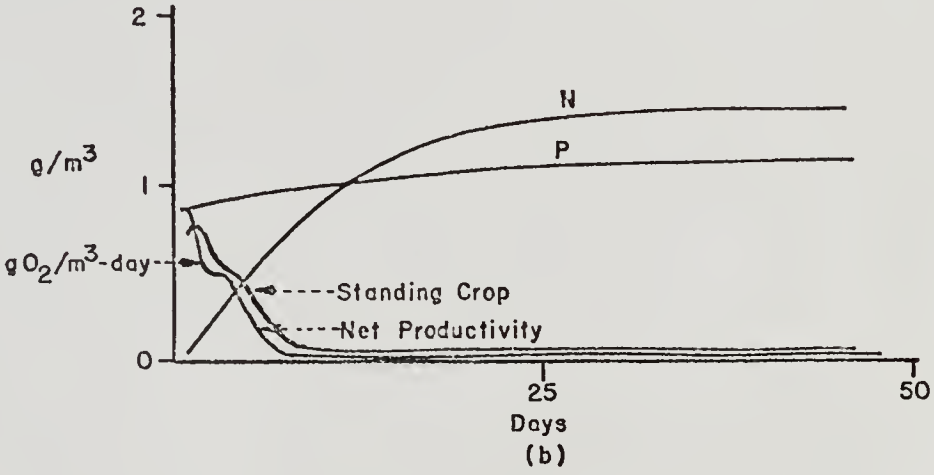
Phosphorus Into Sediment

Figure 32. Simulation of the model in Fig. 25 for increased turbidity (200 ppm) showing stocks and net productivity with time.

a. Nitrogen input (J_3) corresponded to that in Fig. 27 (0.15 g/m^3 input with 0.058 g/m^3 steady state stock for Q_1) resulting in a new nitrogen stock of 0.44 g/m^3.

b. Nitrogen input (J_3) corresponded to that in Fig. 28b (1.6 g/m^3 input with 0.21 g/m^3 steady state stock for Q_1) resulting in a new nitrogen stock of 1.46 g/m^3.


2
g/m3
1
P
----Standing Crop
gO2/m3-day
-----Net Productivity
N
0
25
50
DAYS
(a)


2
N
g/m3
P
1
gO2/m3-day
----Standing Crop
----Net Productivity
0
25
50
Days
(b)

production, levels of unused nitrogen increased sharply (0.44 g/m^3 and 1.46 g/m^3 for Figs. 32a and b respectively). If turbidity were increased to five hundred parts per million as does happen in the estuary, unused nitrogen concentrations could be extremely high.

Phosphorus in Peninsular Florida

The effect of man on the cycle of phosphorus in peninsular Florida was evaluated by quantitative comparison of man-induced flows with those unaffected by man. Figure 33 shows the major storages and flows in peninsular Florida defined by the Suwannee River on the northwest and by state boundaries everywhere else. Table 6 has each flow, its value, and sources of data. Data are uneven with some correct only to orders of magnitude. A detailed discussion of the derivation of each number is given in Appendix A, which includes the notes to Table 6.

Notes on the Calculations

Only the active portion of sediment or soil (uppermost five feet) was included in the phosphorus storages for natural lands, croplands, lake sediment, and estuarine sediment. Pastureland was included as part of natural lands because it does not receive as heavy energy subsidies (e.g., fertilizers) as cropland. Groundwater (Q_8) was defined only as the main Florida Aquifer; the small shallow aquifers

Figure 33. A quantitative model of phosphorus in peninsular Florida (Fig. 1). Values in the storage tanks are in milligrams per square meter; values on the lines are in milligrams per square meter per year. Circled numbers refer to the description on Table 6 and derivation in Appendix A.

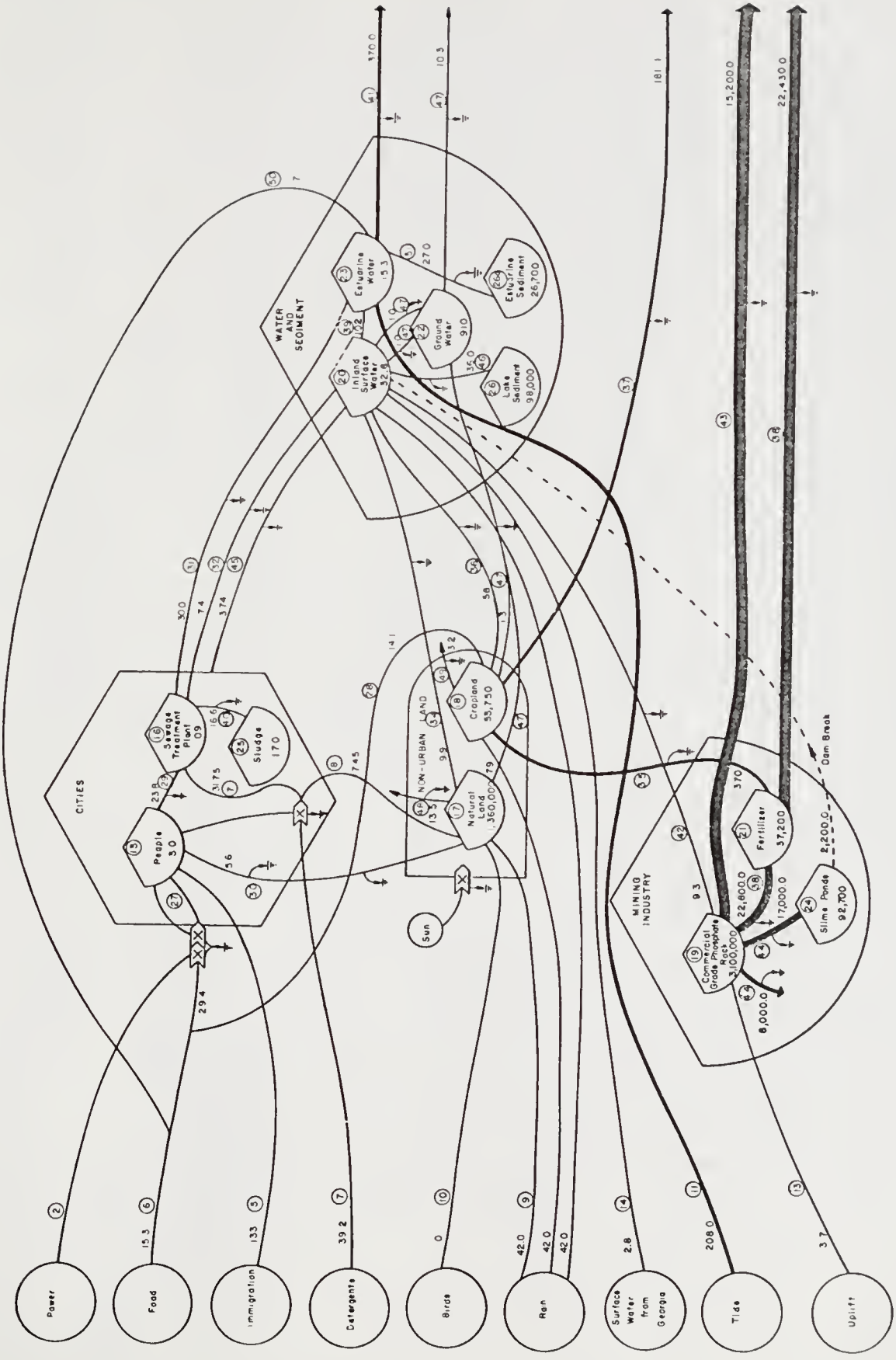

Power
Food
Immigration
Detergents
Birds
Rain
Surface Water from Georgia
Tide
Uplift
CITIES
People 3.0
Sewage Treatment Plant 0.9
Sludge 170
WATER AND SEDIMENT
Estuarine Water 15.3
Estuarine Sediment 26,700
Inland Surface Water 22.4
Ground Water 910
Lake Sediment 98,000
NON-URBAN LAND
Natural Land 1,360,000
Croplands 33,750
Sun
MINING INDUSTRY
Commercial Grade Phosphate Rock 3,100,000
Fertilizer 37,200
Slime Ponds 92,700
Dam Break
294
745
141
9.3
208.0
42.0
42.0
2.8
0
39.2
15.3
13.3
3.7
181.1
170.0
10.3
15,200.0
22,430.0
22,800.0
17,000.0
8,000.0
8,200.0
370

Table 6

Sources, Storages, and Rates for the Peninsular Florida System (Fig. 33)

Pathway on Fig. 33 and Note	Description	Numerical Value	Source
2	Power to the people in the cities	316.4 kilocal/m^2/yr	Fla. Stat. Abst. (1971)
5	Net immigration rate to Florida	.133 mg/m^2/yr	Fla. Stat. Abst. (1971)
6	Phosphorus in the food imported to the study area	15.3 mg/m^2/yr	Stumm and Zollinger (1972) Fla. Stat. Abst. (1971)
7	Phosphorus in detergents imported to the study area	39.2 mg/m^2/yr	Vollenweider (1970)
7	Phosphorus from detergents to sewage treatment plants	31.75 mg/m^2/yr	Vollenweider (1970) Inv. Sewerage Systems (1966) Fla. Stat. Abst. (1971)
8	Phosphorus from detergents imported into septic tanks	7.45 mg/m^2/yr	Inv. Fla. Sewerage Systems (1966)
9	Phosphorus to the land and inland waters from rain	42.0 mg/m^2/yr	Brezonik et al. (1969)
10	Phosphorus brought from the marine to the terrestrial environment by birds	0	Johnston (personal communication)

Table 6 (continued)

Pathway on Fig. 33 and Note	Description	Numerical Value	Source
11	Phosphorus brought into the estuaries with incoming tide	208 $mg/m^2/yr$	U.S. Dept. Commerce (1972) U.S. Army Corps. Eng. (1971) Graham (1954) Alberts et al. (1970)
13	Uplift exposing new commercial grade phosphatic rock	3.7 $mg/m^2/yr$	Cooke (1945)
14	Phosphorus entering the study area through surface streams from Georgia	2.8 $mg/m^2/yr$	U.S. Geol. Surv. (1968)
15	Phosphorus stored in the population of the study area	5.03 mg/m^2	Lehninger (1970) Fla. Stat. Abst. (1971)
16	Phosphorus stored in the sewage treatment plants	.094 mg/m^2	Fla. Stat. Abst. (1971)
17	Phosphorus stored in "naturally" vegetated areas	1,360,000 mg/m^2	Blue (personal communication) Gammon et al. (1953) Steward (1971)
18	Phosphorus stored in cropland	55,750 mg/m^2	Westgate et al. (1957)

Table 6 (continued)

Pathway on Fig. 33 and Note	Description	Numerical Value	Source
19	Phosphate rock having the potential to be mined	3.1×10^6 mg/m^2	U.S. Bureau of Mines. (1969) Env. Prot. Agency (1971a)
20	Phosphorus stored in the surface waters of the study area	32.6 mg/m^2	Fla. Stat. Abst. (1971) Odum (1951)
21	Phosphorus stored in fertilizer	3.72×10^4 mg/m^2	Vollenweider (1970) Sweeney and Maxwell (1969)
22	Phosphorus stored in groundwater	910 mg/m^2	Odum (1951) Fla. Geol. Surv.
23	Phosphorus stored in Florida's estuarine water	15.35 mg/m^2	U.S. Dept. Commerce (1972) Odum (1951) U.S. Army Corps Eng. (1971)
24	Phosphorus stored in the slime ponds of the mining district	92,700 mg/m^2	Specht (1950 Toler (1967)
25	Phosphorus stored in the sludge from sewage treatment plant	166 mg/m^2	
26	Phosphorus stored in lake sediment	98,000 mg/m^2	Schneider and Little (1969) Brezonik et al. (1969)

Table 6 (continued)

Pathway on Fig. 33 and Note	Description	Numerical Value	Source
26a	Phosphorus stored in estuarine sediment	26,700 mg/m^2	Huang and Goodell (1967) Fed. Wat. Poll. Cont. Adm. (1969) Miller (1952)
27	Total phosphorus consumed by people in food	29.4 mg/m^2 yr	Stumm and Zollinger (1972) Inv. Sewerage Systems (1966) Fla. Stat. Abst. (1971)
28	Phosphorus from crops grown in Florida to Floridians for consumption	14.1 $mg/m^2/yr$	Jack Moore (Fla. Farm Bureau, personal communication)
29	Phosphorus from human waste to sewage treatment plant	23.8 $mg/m^2/yr$	Stumm and Zollinger (1972) Inv. Sewerage Systems (1966) Fla. Stat. Abst. (1971)
30	Phosphorus from human waste to septic tanks	5.6 $mg/m^2/yr$	Stumm and Zollinger (1972) Inv. Sewerage Systems (1966)

Table 6 (continued)

Pathway on Fig. 33 and Note	Description	Numerical Value	Source
31	Phosphorus from sewage treatment plants to the estuaries	30.0 $mg/m^2/yr$	Inv. of Sewerage Systems (1966) Fla. Stat. Abst. (1971)
32	Phosphorus from sewage treatment plants to inland surface waters	7.4 $mg/m^2/yr$	Stumm and Zollinger (1972) Inv. Fla. Sewerage Systems (1966)
34	Phosphorus from natural soils to surface water through erosion	9.9 $mg/m^2/yr$	Brezonik et al. (1969)
35	Phosphorus from fertilizers applied to cropland	370 $mg/m^2/yr$	NeSmith (1968-1971)
36	Phosphorus from agricultural soil to surface waters	58 $mg/m^2/yr$	Brezonik et al. (1969) Biggar and Cory (1969) Heaney et al. (1971)
37	Phosphorus from crops exported from the state	181.1 $mg/m^2/yr$	Fla. Almanac (1972) Donahue et al. (1971) Howard et al. (1962)
38	Phosphorus from phosphate rock mined to fertilizers	22,800 $mg/m^2/yr$	U.S. Bureau of Mines (1969)

Table 6 (continued)

Pathway on Fig. 33 and Note	Description	Numerical Value	Source
38	Phosphorus from fertilizers exported from the state	18,700 $mg/m^2/yr$	Donahue et al. (1971) U.S. Bureau of Mines (1969)
39	Phosphorus from surface water into estuaries	102.0 $mg/m^2/yr$	Pyne et al. (1967) Sheffield (1970)
40	Phosphorus from sewage treatment plants into sludge	16.6 $mg/m^2/yr$	Am. Chem. Soc. (1969)
41	Phosphorus from estuaries to ocean	370 $mg/m^2/yr$	Odum (1951) U.S. Dept. Commerce (1972) U.S. Army Corps Eng. (1971)
42	Phosphorus from mining wastes to Peace and Alafai Rivers (surface waters)	9.3 $mg/m^2/yr$	Lanquist (1953) Specht (1950)
43	Unprocessed phosphate rock exported from the state	15,200 $mg/m^2/yr$	U.S. Bureau of Mines (1970)
44	Phosphorus from mining operations into slime holding ponds	17,000 $mg/m^2/yr$	Env. Prot. Agency (1971a)

Table 6 (continued)

Pathway on Fig. 33 and Note	Description	Numerical Value	Source
44	Phosphorus loss through washer and flotation operations other than to slime ponds	8,000 $mg/m^2/yr$	Env. Prot. Agency (1971b)
45	Urban runoff	3.74 $mg/m^2/yr$	Weibel et al. (1969)
46	Net P deposition in lake sediments	3.6 $mg/m^2/yr$	Stumm (1972) Vollenweider (1970)
47	Phosphorus from cropland to groundwater	1.3 $mg/m^2/yr$	Odum (1951) Sheffield (1970) Pyne (1967)
47	Phosphorus from natural lands to groundwater	7.9 $mg/m^2/yr$	Ibid.
47	Phosphorus from surface waters to groundwater	1.0 $mg/m^2/yr$	Ibid.
47	Phosphorus from groundwater to surface water (springs)	1.0 $mg/m^2/yr$	Ibid.
47	Phosphorus from groundwater to ocean	10.3 $mg/m^2/yr$	Ibid.
48	Phosphorus to air from natural lands through fire	13.5 $mg/m^2/yr$	Steward (1971)

Table 6 (continued)

Pathway on Fig. 33 and Note	Description	Numerical Value	Source
49	Phosphorus to air from cropland through dust blowing	3.2 $mg/m^2/yr$	Schneider and Little (1969)
50	Phosphorus taken out of the estuaries with fish harvest	.68 $mg/m^2/yr$	Fla. Stat. Abst. (1971) Vollenweider (1970)
51	Net phosphorus flux to estuarine sediment	27 $mg/m^2/yr$	Pomeroy (1972)

around the state were neglected. Commercial grade phosphate rock includes only phosphate rock that is the grade considered presently economical to mine (6.2% P).

For lack of data, some numbers are more reliable than others. Three numbers in particular are questionable although the order of magnitude may be correct. The phosphorus in runoff from cropland to lakes and rivers (58 mg/m^2/year on Fig. 33) is quite variable. Brezonik and Shannon (1971) gave values which, when converted to the units of Fig. 33, range from 2.1 to 15.7 mg/m^2/year and Heaney et al. (1971) gave a value for the truck farming district of Florida of 2,134.4 mg/m^2/year. Biggar and Cory (1969) give national averages for agricultural land fertilized in a similar manner as Florida's cropland of 65.0 to 267 mg/m^2/year. The often-quoted phosphorus concentration of runoff from fertilized cropland is 1 mg/1 or 47 mg/m^2/year for Florida. The value used here of 58 mg/m^2/year is a weighted average since runoff from the peat in the truck farming district is quite high, but runoff in other areas is much lower (Brezonik and Shannon, 1971, vs. Heaney et al., 1971).

Also uncertain are the losses of phosphorus to the air from natural land and cropland. The Southeastern Forest Fire Laboratory in Macon, Georgia, is attempting now to make some measurements on the phosphorus in smoke from forest fires to determine in particular the quantity of nutrients in smoke which do not fall back immediately but

are later "rained out." The number (13.5 mg/m^2/year) calculated here is based on the amount of biomass burned multiplied by its phosphorus content. In cropland, phosphorus may be blown up into the air in dust after heavy fertilization.

For overall perspective several unit area summary diagrams are given (Figs. 34 and 35). Due to mining, Florida is losing phosphorus 125 times faster than it is gaining it (Fig. 34a). Neglecting the mining industry and the crops exported, the input of phosphorus is about the same as the output (Fig. 35a) or 307 mg/m^2/year input versus 380 mg/m^2/year output.

Note that input and output from the tide dominate the "natural" flows. Inputs from rain and from detergents are presently the same. Florida exports six times more phosphorus in food than it consumes (181 mg/m^2/year exported and 29.4 mg/m^2/year consumed).

Residence times with respect to various fluxes may be significant. With respect to the total inputs and outputs (Fig. 34a), Florida has a 125-year reserve of phosphorus. The reserve of commercial grade rock it has is 50 years. Keeping in mind a possible geologic source of phosphorus for Florida, the residence time of phosphorus with respect to tidal input alone is about 20,000 years and with respect to the input from rain is 100,000 years (4,734,283 mg/m^2 ÷ 208 and 42 mg/m^2/year respectively). Both figures may

Figure 34. Unit area diagrams summarized from the model in Fig. 33.

a. Sum of all inputs, storages, and outputs.

b. Components of inputs, outputs, and recycle pathways.

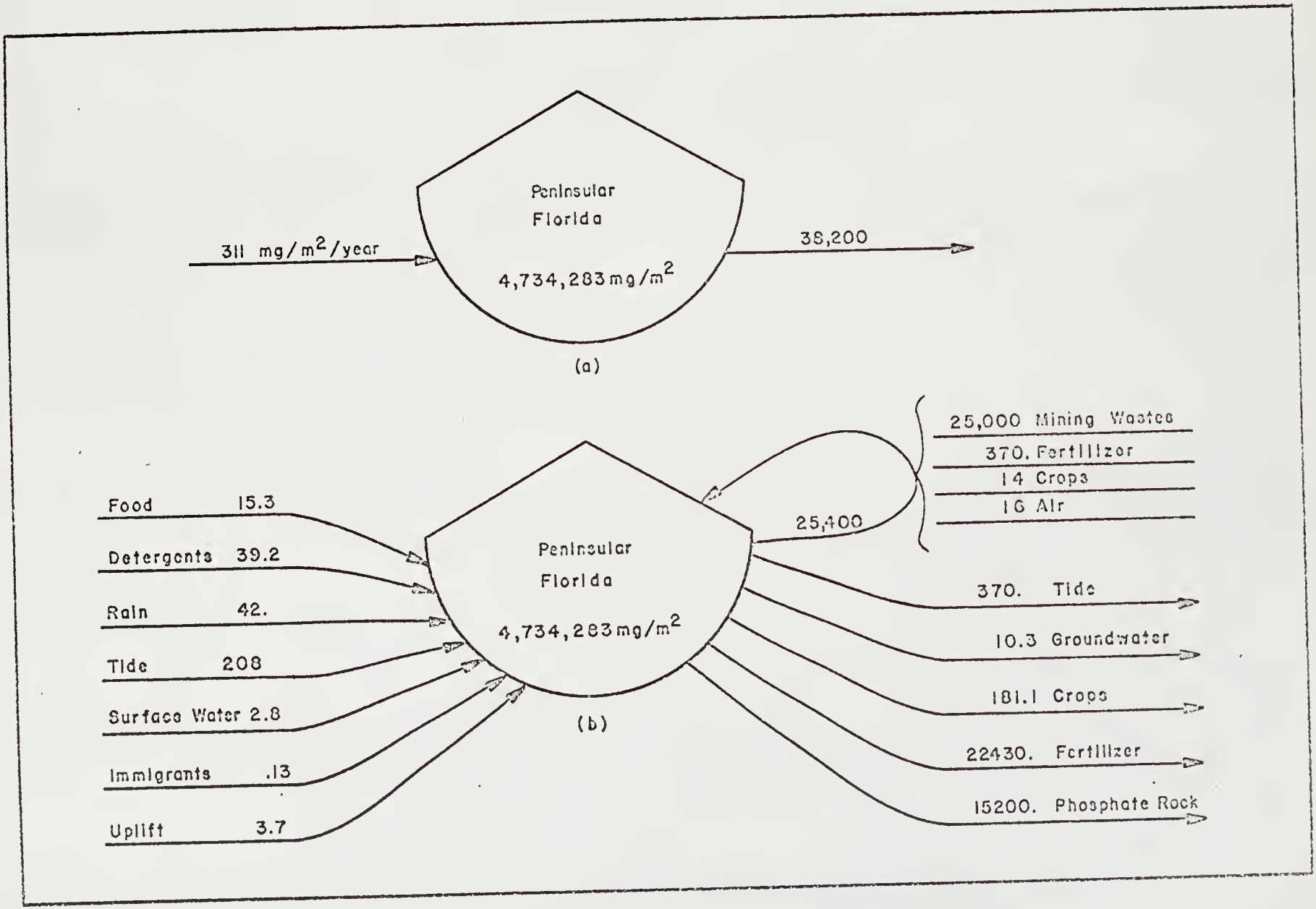
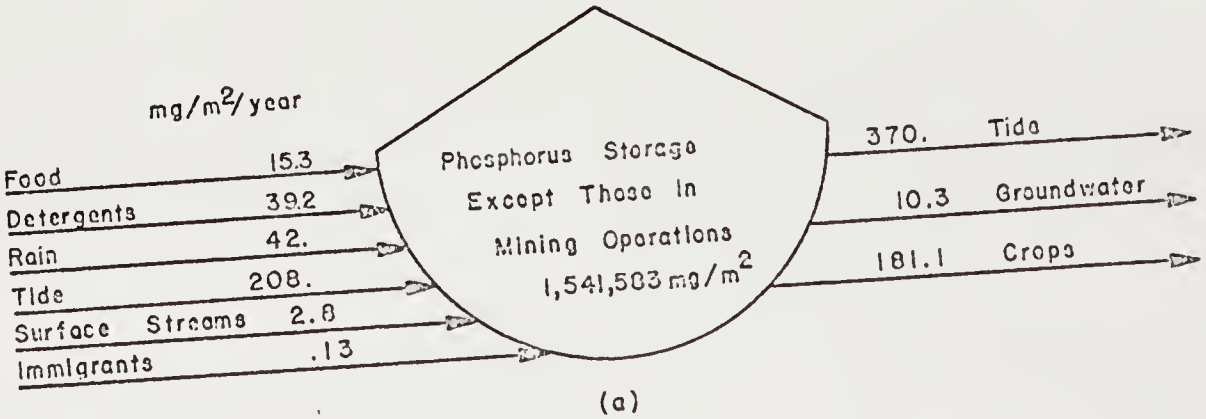

Peninsular
Florida
4,734,283 mg/m²
311 mg/m²/year
38,200
(a)
Food 15.3
Detergents 39.2
Rain 42.
Tide 208
Surface Water 2.8
Immigrants .13
Uplift 3.7
Peninsular
Florida
4,734,283 mg/m²
(b)
25,000 Mining Wastes
370. Fertilizer
14 Crops
16 Air
25,400
370. Tide
10.3 Groundwater
181.1 Crops
22430. Fertilizer
15200. Phosphate Rock

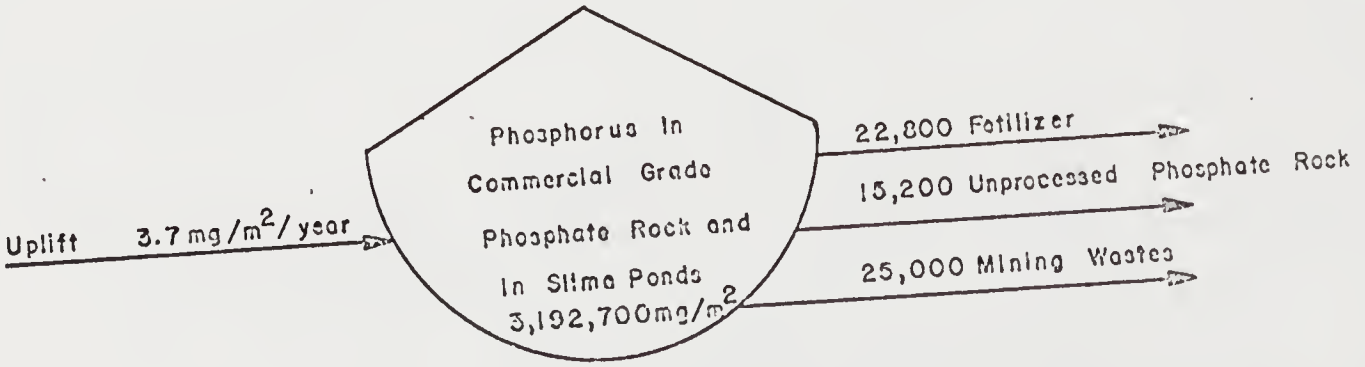
Figure 35. Unit area diagrams summarized from the model in Fig. 33.

a. Inputs, outputs, and storages of phosphorus for the peninsula from all sources except mining.

b. Input, outputs, and storage of phosphorus for all processes associated with the phosphate rock mining industry.


mg/m²/year
Food 15.3
Detergents 39.2
Rain 42.
Tide 208.
Surface Streams 2.8
Immigrants .13
Phosphorus Storage Except Those In Mining Operations 1,541,583 mg/m²
370. Tide
10.3 Groundwater
181.1 Crops

(a)


Uplift 3.7 mg/m²/year
Phosphorus In Commercial Grade Phosphate Rock and In Slime Ponds 3,192,700mg/m²
22,800 Fetilizer
15,200 Unprocessed Phosphate Rock
25,000 Mining Wastes

(b)

vary depending on the phosphorus levels in seas around Florida due to upwelling regimes.

Further observations can be made from examination of the complete model (Fig. 33). Note that a great many of the phosphorus flows are in the range of 10 to 40 $mg/m^2/year$. These include flows generally considered natural (e.g., land drainage and rain) and flows generally considered man-induced (e.g., detergents and sewage effluent). River run-off, tidal input and output, and flows associated with agriculture are higher (100 to 300 $mg/m^2/year$). The exports of the mining industry are two orders of magnitude higher still than these. The impact of a slime spill is readily observable from the dashed line showing a spill equal in magnitude to the Cities Service spill of December, 1971, into the Peace River (Alberts et al., 1972).

This large system may be storing nutrients in the lakes and estuaries. Indications are that the percent of phosphorus in lake sediment and in most estuarine sediment is about the same (0.02 to 0.05% P or 90 to 220 g/m^3 phosphorus). Higher values are found in those estuaries which receive the drainage from the phosphorus district.

Phosphorus concentration in the sediments of Charlotte Harbor and Hillsborough Bay is 0.63% or about 2,800 g/m^3. For comparison, elemental phosphorus in commercial grade rock is 6.2% or 80,600 g/m^3 (rock weighs more than sediments, thus the latter is not simply 10 times larger than

the former as the percentage ratio would indicate). At the assumed rate of sedimentation the upper five feet of lake and estuarine sediment under consideration has taken 2,700 and 1,000 years respectively to accumulate. Since rates of sedimentation are somewhat conjectural, a sedimentation rate of five feet per several thousand years is a good estimate.

Deposition of Phosphorus in Florida Over Geologic Time

As first summarized by Sellards (1913) and discussed in detail in the introduction, various mechanisms for phosphorus deposition have been proposed. These include phosphates derived from the mineralization of guano, concentrations from phosphatic skeletons and teeth, and selective redeposition from solutions. Although the apatite compounds found in phosphate rock vary considerably with fluor-apatite [$3Ca_3(PO_4)_2 \cdot CaF_2$] and tricalcium phosphate [$Ca(PO_4)_2$] being the most common, calculations for this report are based on the molecular weight of $CaPO_4$, which is an ion but represents the first stages in forming an apatite crystal. Whenever the term calcium phosphate is used here, it means $CaPO_4$; similarly, $CaPO_4$ is used as an abbreviation for all forms of apatite.

Data Evaluation

Figure 36 is a model of processes which may have been important in forming phosphate deposits. It shows the chemical equilibria and sources of ions to the system. The stoichiometry is given in conventional form in Fig. 37. Note

Figure 36. Energy circuit model of sources and geochemical reactions for dissolution and reprecipitation of calcium carbonate and calcium phosphate in Florida. All chemical reaction pathways are two-directional, but only the pathways which indicate normal direction of net changes are shown (see Fig. 37). Inset is an overall simplification.

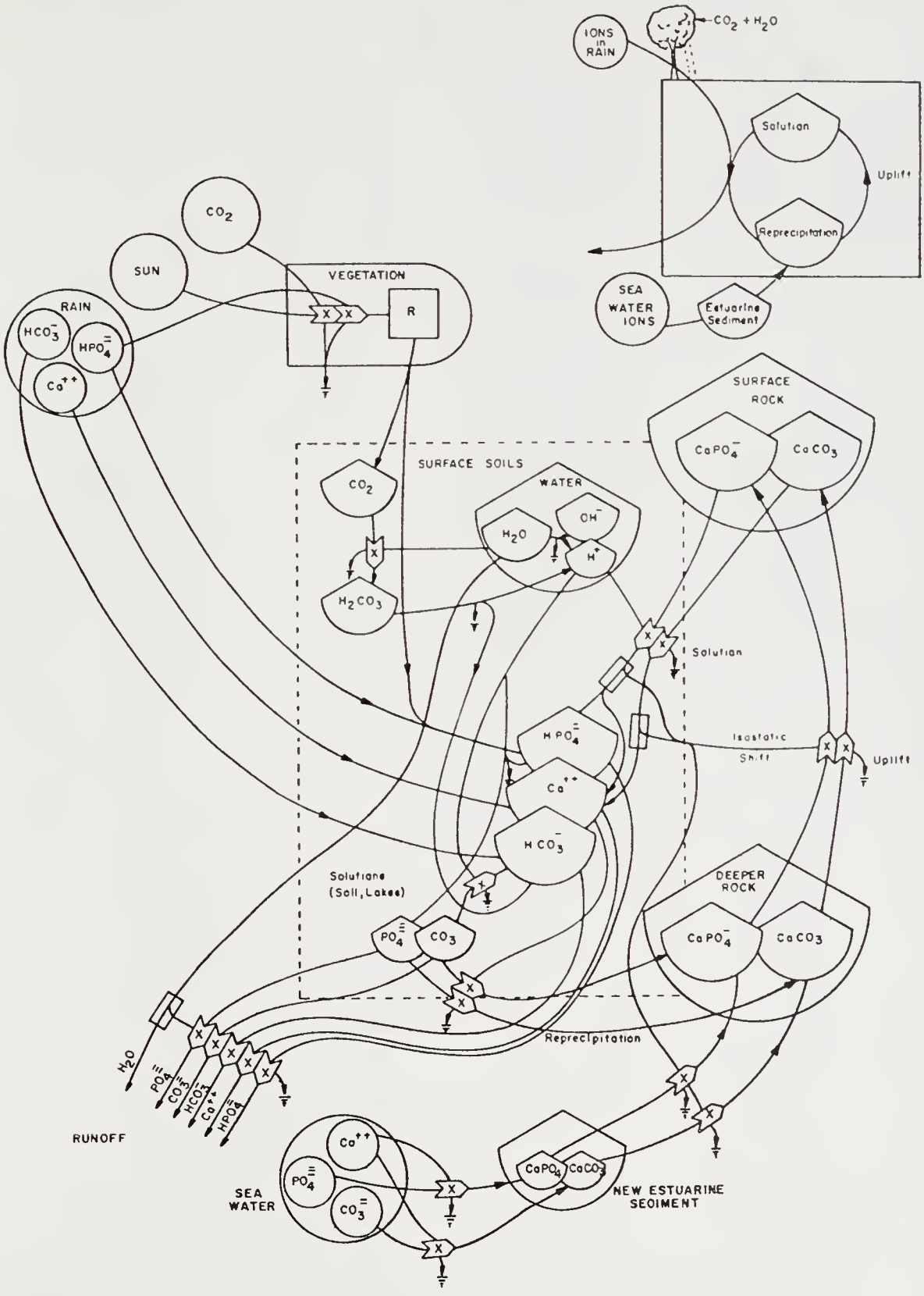

IONS in RAIN
$CO_2 + H_2O$
Solution
Uplift
Reprecipitation
SEA WATER IONS
Estuarine Sediment
CO_2
SUN
VEGETATION
R
RAIN
HCO_3^-
$HPO_4^=$
Ca^{++}
SURFACE ROCK
$CaPO_4^-$
$CaCO_3$
SURFACE SOILS
WATER
H_2O
OH^-
H^+
H_2CO_3
Solution
Isostatic Shift
Uplift
$HPO_4^=$
Ca^{++}
HCO_3^-
Solutions (Soil, Lakes)
DEEPER ROCK
$CaPO_4^-$
$CaCO_3$
$PO_4^=$
$CO_3^=$
Reprecipitation
H_2O
$PO_4^=$
$CO_3^=$
HCO_3^-
Ca^{++}
$HPO_4^=$
RUNOFF
Ca^{++}
$PO_4^=$
$CO_3^=$
SEA WATER
$CaPO_4$
$CaCO_3$
NEW ESTUARINE SEDIMENT

Figure 37. Stoichiometry of the chemical equilibria and overall process of dissolution and selective redeposition of calcium carbonate and calcium phosphate for the model in Fig. 36.

STOICHIOMETRY of PROCESS MODELED

(a) Equilibria Under Consideration

1. $H_2O + CO_2 \rightleftharpoons H_2CO_3 \rightleftharpoons H^+ + HCO_3^-$

H^+

$+$

$CO_3^= + Ca^{++} \rightleftharpoons CaCO_3$ → several mineral forms, ultimately calcite

2. $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$

H^+

$+$

$HPO_4^= \rightleftharpoons H^+ + PO_4^=$

$+$

Ca^{++}

$CaPO_4^-$ → various mineral forms, ultimately apatites

(b) Overall Process

1. $H_2O + CO_2 + CaCO_3 \rightleftharpoons 2HCO_3^- + Ca^{++}$

2. $H^+ + CaPO_4^- \rightleftharpoons HPO_4^= + Ca^{++}$

that the overall process shows the products of biological respiration in the soil driving the dissolution of $CaCO_3$ and $CaPO_4$. Although much of the CO_2 produced diffuses into the air, some reacts with water to form hydrogen ions and bicarbonate ions. The acidity associated with the hydrogen ions is then available to dissolve $CaCO_3$ and $CaPO_4$ in accordance with the equilibrium condition of the interstitial water. As the water percolates through the soil and rock, it becomes more basic and the equilibrium shifts so that $CaCO_3$ and $CaPO_4$ are now precipitated. Added to these ions in solution are those contributed by rain. The ratio of ions in solution in the surface water versus those that ultimately reach the groundwater indicates that the percent of $CaPO_4$ reprecipitated versus that initially dissolved is greater than the percent of $CaCO_3$ reprecipitated versus the amount of it initially dissolved. The implication is that $CaPO_4$ relative to $CaCO_3$ becomes enriched in the subsoil. Specifically, as shown in Table 7, the concentrations of Ca^{++} and HCO_3^- in groundwater are higher than they are in surface water indicating overall losses for these two ions, but the concentration of phosphorus in groundwater is lower than in surface water indicating overall precipitation.

The insert diagram (Fig. 36) illustrates the physical processes under consideration; it enables clearer understanding of the countercurrent phenomena of percolation downward and isostatic adjustment upward, keeping the shelf

Table 7

Ionic Concentrations in Florida's Surface Waters and Groundwater, mg/l

Ion	Surface Waters	Groundwater
Ca^{++}	10	70
HCO_3^-	80	200
P	0.1	0.05

area in near equilibrium. Entering the system from the air, carbon dioxide required for photosynthesis is used by plants to generate organic material which is respired in the soil producing H_2O and CO_2, some of which is converted to H^+ and HCO_3^- ions. The acidity then dissolves the $CaCO_3$ and $CaPO_4$ which is then reprecipitated in some different ratio as the water becomes basic. As water percolates downward, deeper rock is slowly moving upward at a rate of 0.01 to 0.07 m/1,000 years (Rusnak, 1967); new estuarine sediment becomes rock and enters the system. The ratio of $CaCO_3$ to $CaPO_4$ in new rock can vary depending on the conditions under which it was deposited.

The overall process of solution and redeposition can theoretically lead to either a gain or loss in total rock mass depending on the inflows of new calcium, carbonate, and phosphate. Note that (Fig. 36) there are two possible

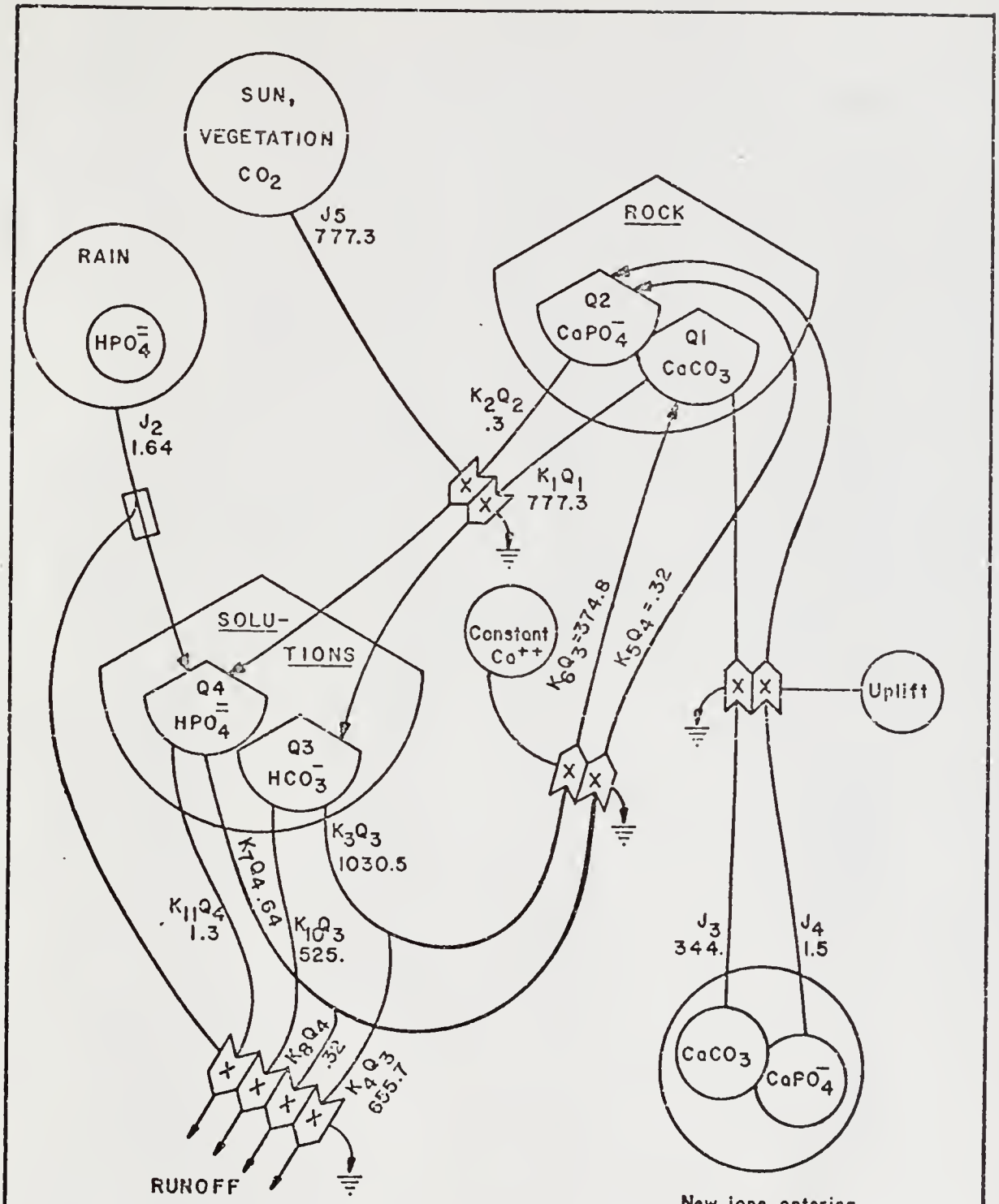
sources of phosphorus outside the system -- phosphorus in rain and phosphorus in sea water entering the sites of estuarine deposition. In either case, the ultimate source of the phosphorus to the land must be the ocean.

It has been established that the ions in seawater are transported from the ocean to the land through rain. High winds and strong oceanic currents may have prevailed during Pleistocene glacial stages so that Florida could have been subject to more upwelling and exchange inducing higher phosphorus from rain from marine air masses. For simulation purposes here it was assumed that the maximum possible phosphorus input from rain was 254 mg/m^2/year (100 inches at .1 mg/l). It is presently between 38 and 50 mg/m^2/year (50 inches at .03 to .04 mg/l).

Estuarine deposits rich in phosphorus are the other possible source outside the system. If nutrient upwelling from deep ocean waters occurred along the continental slope, lateral eddy diffusion could bring this phosphorus into estuaries. The possible magnitude of this flux was evaluated here for a hypothetical upwelling zone one hundred miles off the coast of western Florida. Turbulent eddy diffusivity and velocities are based on the present circulation pattern of the Eastern Gulf of Mexico. Brooks' (1960) solution to the continuity equation $\frac{\partial}{\partial y}(-Ey\ \frac{\partial c}{\partial x})+U\ \frac{\partial c}{\partial x} = 0$ (Appendix C) with advection along the loop current and lateral eddy diffusion toward Florida was used to calculate the flux to Florida. For a

surface water phosphorus concentration along the upwelling zone of .03 mg/l (characteristic of the Peruvian upwelling zones), a possible flux of 400 mg/m^2/year "extra" elemental phosphorus into what is now Florida was obtained. The mechanism for concentrating and depositing the phosphorus could be marine organisms such as clams and fish or it could be birds through guano deposits. Whatever it is, the maximum amount available depends on the transport to Florida by rain and by currents. In Fig. 38 is a simplification of Fig. 36 for analog simulation. Table 8 gives numerical values and sources of data for each flow and storage. The notes to Table 8 included in Appendix A discuss each numerical value in detail. Numerical values and mathematical functions for the model given in Fig. 38 represent the $CaCO_3$ and $CaPO_4$ in the top one hundred feet of soil and rock (Q_1 and Q_2) being dissolved due to the acidity produced from biological respiration. Some of the ions in solution (Q_3 and Q_4) are exported from the system through surface runoff and groundwater and some are reprecipitated as $CaCO_3$ and $CaPO_4$. Since there is apparently a large amount of calcium available for reprecipitation, for the purpose of analog simulation it was treated as an outside source which does not limit the precipitation process. Within the pH range of surface and percolating water most of the carbonate exists as HCO_3^- and most of the phosphate exists as $HPO_4^{=}$; therefore, only these ionic species were considered in the simplified model.

Figure 38. Simplified geochemical phosphorus model used for simulation (see more complex version in Fig. 36). Included are the mathematical terms for each flux and their numerical values. Units are millimoles per square meter (100' depth) for storages and millimoles per square meter per year for rates. Translation into differential equations is made below.



$$\dot{Q}_1 = J_3 + K_6Q_3 - K_1Q_1$$

$$\dot{Q}_2 = J_4 + K_5Q_4 - K_2Q_2$$

$$\dot{Q}_3 = J_5 + K_1Q_1 - K_3Q_3 - K_{10}Q_3$$

$$\dot{Q}_4 = J_2 + K_2Q_2 - K_7Q_4 - K_{11}Q_4$$

Table 8

Sources, Storages, and Rates for Deposition of Phosphorus System (Fig. 38)

Mathematical Expression	Note	Description	Numerical Value ($mmoles/m^2/year$)	Source
Q_1	1	$CaCO_3$ in uppermost 100' of soil and rock	35.6×10^7 $mmoles/m^2$	Cooke (1945)
Q_2	2	$CaPO_4$ in uppermost 100' of soil and rock	$.29 \times 10^7$ $mmoles/m^2$	Cooke (1945)
Q_3	3	HCO_3^- percolating through the uppermost 100' of soil and rock	655.7 $mmoles/m^2$	U.S. Geol. Surv. (1961-1968)
Q_4	4	$HPO_4^{=}$ percolating through the uppermost 100' of soil and rock	.625 $mmoles/m^2$	Odum (1951)
J_2	5	$HPO_4^{=}$ in rain	1.64	Bradley (1972) Brezonik et al. (1969) Schneider and Little (1969)
J_3	6	$CaCO_3$ contribution from uplift due to isostatic adjustment	350.0	Back calculated
J_4	7	$CaPO_4$ contribution from uplift due to isostatic adjustment	1.5	Back calculated

Table 8 (continued)

Mathematical Expression	Note	Description	Numerical Value (mmoles/m^2/year)	Source
J_5	11	HCO_3^- introduced to the system by respiration of organic material in the soil	777.3	Steady state calculation
K_1Q_1	11	$CaCO_3$ dissolved in the soil and rock	777.3	Ibid.
K_2Q_2	10	$CaPO_4$ dissolved in the soil and rock	.30	Ibid.
K_3Q_3	11	HCO_3^- in percolating water which is either precipitated or exported to the groundwater	1,030.56	Ibid.
K_4Q_3	9	HCO_3^- which is exported to groundwater	655.7	Odum (1957)
K_6Q_3	11	HCO_3^- which is reprecipitated as $CaCO_3$	374.86	Steady state calculation
$K_{10}Q_3$	8	HCO_3^- which is exported through surface runoff	525.0	U.S. Geol. Surv. (1961-1968)
K_7Q_4	10	$HPO_4^=$ in percolating water which is either precipitated or exported to the groundwater	.64	Steady state calculation

Table 8 (continued)

Mathematical Expression	Note	Description	Numerical Value ($mmoles/m^2/year$)	Source
K_8Q_4	9	$HPO_4^{=}$ which is exported to the groundwater	.32	Odum (1957)
K_5Q_4	10	$HPO_4^{=}$ which is reprecipitated as $CaPO_4$	.32	Steady state calculation
$K_{11}Q_4$	8	$HPO_4^{=}$ which is exported through surface runoff	1.3	Odum (1951)

Note that 48% of the $CaCO_3$ dissolved was reprecipitated (374.86/777.3 from Fig. 38) and 106% of the $CaPO_4$ dissolved was reprecipitated (0.32/0.30); that is, all of what was dissolved plus some phosphorus from rain was precipitated in the subsoil.

Uplift rate was assumed to be 0.03 m/1,000 years, which was the rate required to replace the rock lost in runoff and groundwater export. Residence time of phosphorus from reprecipitation and uplift was about 10 million years (0.29×10^7 mmoles/m^2/0.32 mmoles/m^2/year); and from rain was about 1.75 million years (0.29×10^7 mmoles/m^2/1.64 mmoles/m^2/year). Residence time of $CaCO_3$ with respect to reprecipitation and uplift was about one million years (35.6×10^7 mmoles/m^2/375 mmoles/m^2/year).

Simulation Evaluation

Steady State under Initial Conditions

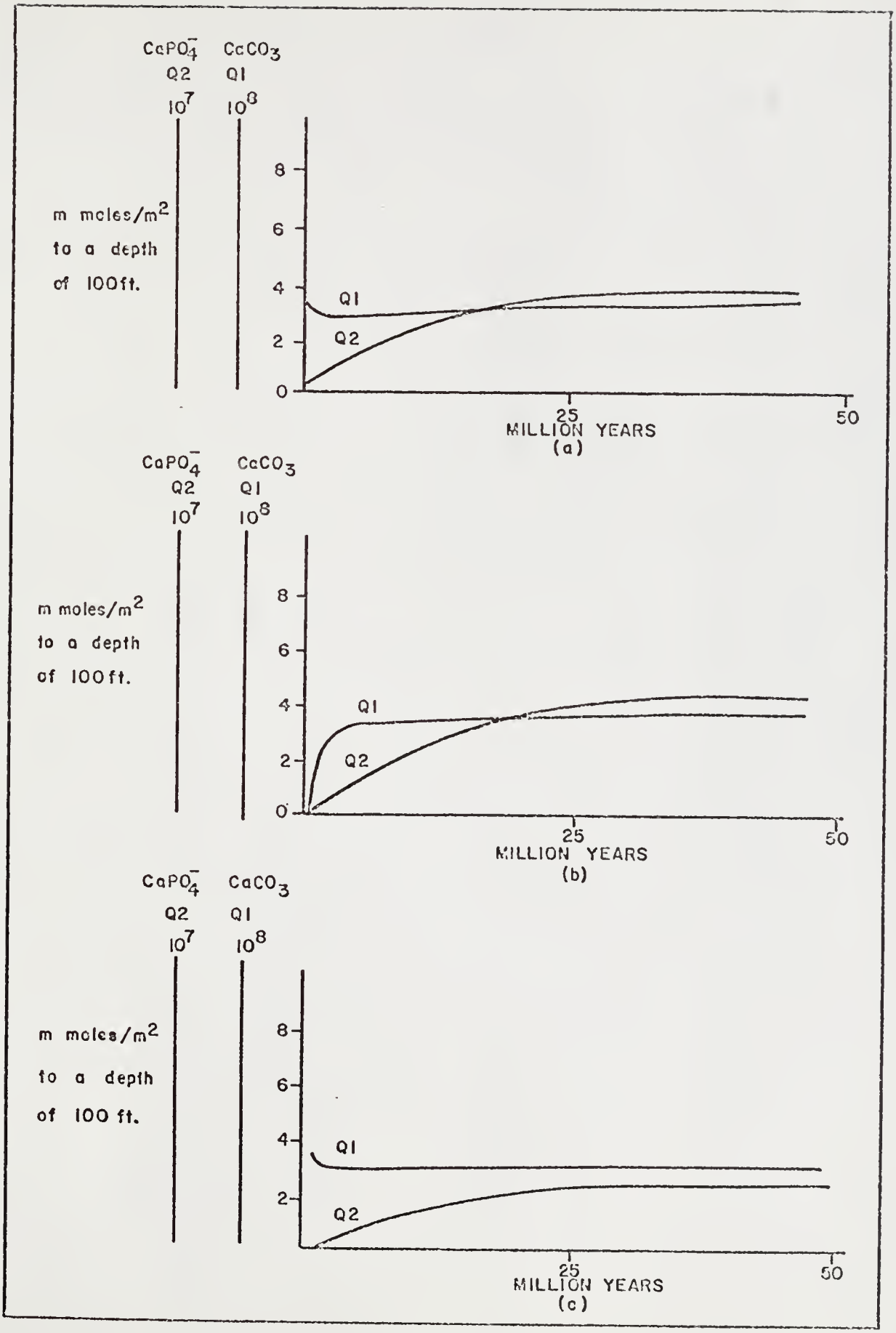
The steady state reached when the simplified model shown in Fig. 38 was simulated is given in Fig. 39a. Note that the steady state concentration of $CaPO_4$ in rock was reached after 25 million years but the steady state $CaCO_3$ concentration was reached in 2 million years. The $CaCO_3$ concentration in rock (Q_1) decreased from 35.6×10^7 to 31.9×10^7 mmoles/m^2 or 31.9×10^9 mg/m^2 and the $CaPO_4$ concentration in rock increased from 0.29×10^7 to 4.0×10^7 mmoles/m^2 or 5.4×10^9 mg/m^2. Initially $CaPO_4$ was 1% of the rock; at steady state it was 14.5%.

Figure 39. Simulation of the geochemical deposition model in Fig. 38 for low starting concentrations of calcium phosphate in rock.

a. The initial calcium phosphate of the rock entering the system is 1% by weight; the steady state content for calcium phosphate (Q_2) is 14.5%.

b. Initial conditions are zero as in rock being uplifted out of the sea. The initial calcium phosphate content of the rock entering the system is 1% and the steady state content of Q_2 is 14.5%.

c. The initial calcium phosphate content of the rock entering the system is 0.5% and the steady state content of Q_2 is 10%.


$CaPO_4^-$
Q2
10^7
$CaCO_3$
Q1
10^8
m moles/m^2
to a depth
of 100ft.
8
6
4
2
0
Q1
Q2
25
50
MILLION YEARS
(a)
$CaPO_4^-$
Q2
10^7
$CaCO_3$
Q1
10^8
m moles/m^2
to a depth
of 100ft.
8
6
4
2
0
Q1
Q2
25
50
MILLION YEARS
(b)
$CaPO_4^-$
Q2
10^7
$CaCO_3$
Q1
10^8
m moles/m^2
to a depth
of 100 ft.
8
6
4
2
Q1
Q2
25
50
MILLION YEARS
(c)

If the initial conditions were zero (Fig. 39b) as they would be when sedimentary rock was being uplifted out of the sea or sea level was being lowered, the same steady state resulted. The land mass increased.

For comparison, the model was simulated, changing the concentration of the $CaPO_4$ in the new rock entering the system from 1% to 0.5%. As indicated in Fig. 39c, the steady state concentration was 10% $CaPO_4$ rather than 14.5% when initial concentration was 1%.

Varying Levels of Phosphorus in Rain

Little change in $CaPO_4$ levels in rock occurred when the amount of rain or the phosphorus in it was varied. Decreasing the rain input to correspond with 15 inches of rain per year at the same phosphorus concentration (.04 mg/1) resulted in a steady state $CaPO_4$ concentration in rock of 13.7% by weight. Increasing the rain input to a very high value corresponding to 100 inches of rain per year at a concentration of .1 mg/1 caused the $CaPO_4$ concentration in rock to increase to 17.5%. In the case of increased rain, the mass of Florida increased 4%. For perspective, note that under the original conditions of the model the steady state $CaPO_4$ concentration was 14.5%. With low rain it was 13.7% and with high rain and high nutrient content in the rain it was 17.5%.

Variations in Rates of Estuarine Rock Entering the System

With no new estuarine rock entering the system, a case in which the present land mass eroded to a low level (Fig. 40a), the concentration of $CaPO_4$ increased from the initial value of 1% to 4.4% of the total rock remaining. The total rock mass decreased from 36.0×10^9 to 12.3×10^9 mg/m^2.

With an increased rate of estuarine rock entering the system to .11 m/1,000 years such as may have occurred during times of increased erosion, the steady state $CaPO_4$ concentration was 13.5% of the total rock mass (Fig. 40b). The total rock mass increased from 36.0×10^9 to 114.3×10^9 mg/m^2.

Reworking the Hawthorn Formation or Guano Deposits as a Source

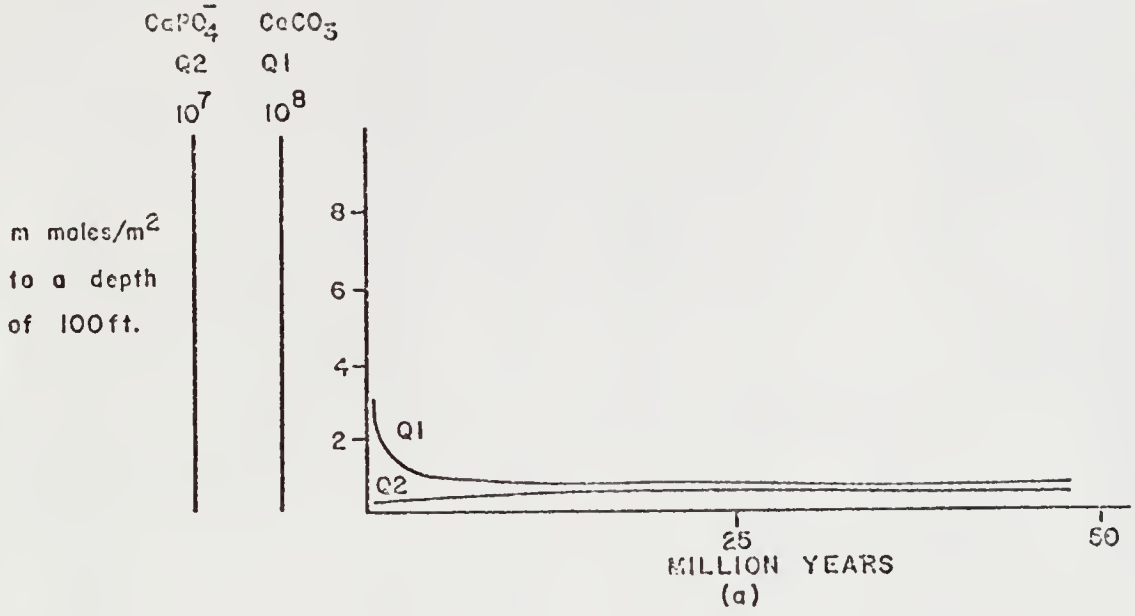
Later Pliocene age phosphate deposits are thought by some to have been formed by concentrating the phosphorus from the Hawthorn formation in terrestrial deposits (Alachua formation) and in coastal type deposits (Bone Valley formation).

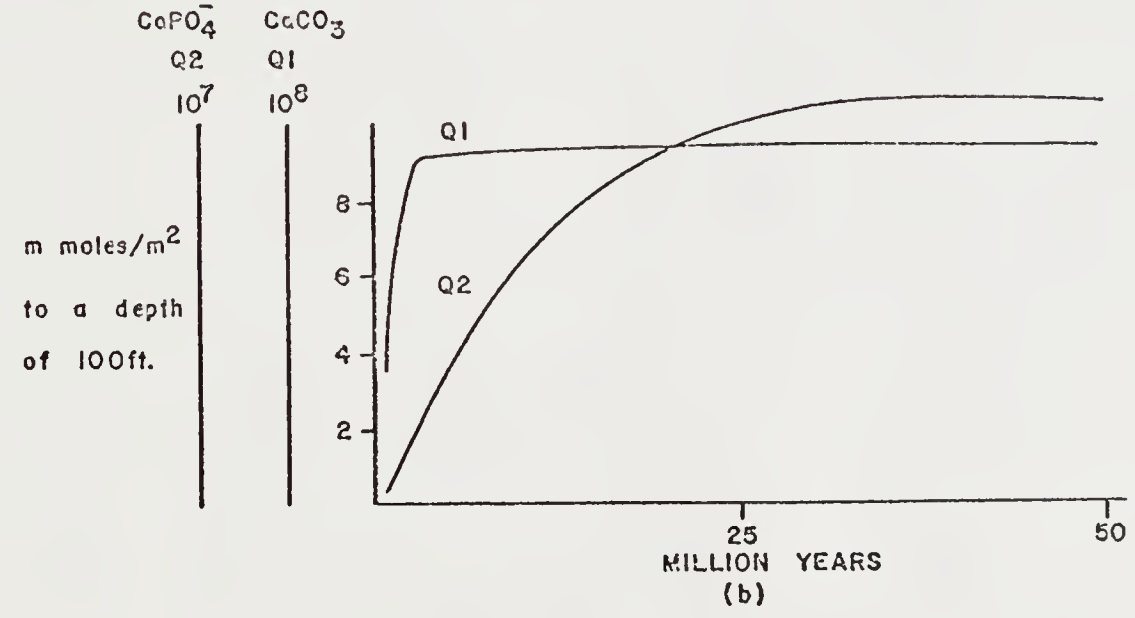
Although concentrating phosphorus from a relatively pure limestone to the Hawthorn formation and finally to the Bone Valley formation is envisioned here as a continuous process, the model simulated (Fig. 38) does not include recycle pathways from land to estuary to land. Therefore, the model was run in discrete stages by changing the ratio of $CaCO_3$ to $CaPO_4$ in the rock entering the system. Figure 41a gives the results of simulation when the $CaPO_4$

Figure 40. Simulation of the geochemical deposition model in Fig. 38 for varying amounts of new estuarine material entering the system.

a. No new material entered the system.

b. New material with a $CaPO_4$ content of 1% entered the system at a rate of .11 m/1,000 years.


$CaPO_4^-$
Q2
10^7
$CaCO_3$
Q1
10^8
m moles/m²
to a depth
of 100ft.
8
6
4
2
Q1
Q2
25
50
MILLION YEARS
(a)


$CaPO_4^-$
Q2
10^7
$CaCO_3$
Q1
10^8
m moles/m²
to a depth
of 100ft.
Q1
Q2
8
6
4
2
25
50
MILLION YEARS
(b)

concentration in new rock was increased to 5%; there is 4 to 17% in the Hawthorn formation (Carr and Alverson, 1959). The steady state $CaPO_4$ content after 25 million years was 40% of the total rock mass. The Bone Valley and Alachua formations which are mined average 31% $CaPO_4$ (Altshuler et al., 1964).

This same simulation (Fig. 41a) can be thought of as a variation which included a large phosphorus contribution from guano deposits on land, the Hawthorn phosphates eroded and cycled into the estuaries being the birds phosphorus source. The numerical value of J_4 (Fig. 38) used for this simulation was 15 mmoles/m^2/year $CaPO_4$ or 2,025 mg/m^2/year. This corresponded to an input from guano of 465 mg elemental phosphorus/m^2/year. Bird Islands in the Pacific contribute from 1.2×10^6 mg/m^2/year to 10.0×10^6 mg/m^2/year elemental phosphorus to the land (Hutchinson, 1950; Coker, 1935; and Murphy, 1927).

Upwelling as a Source of Phosphorus

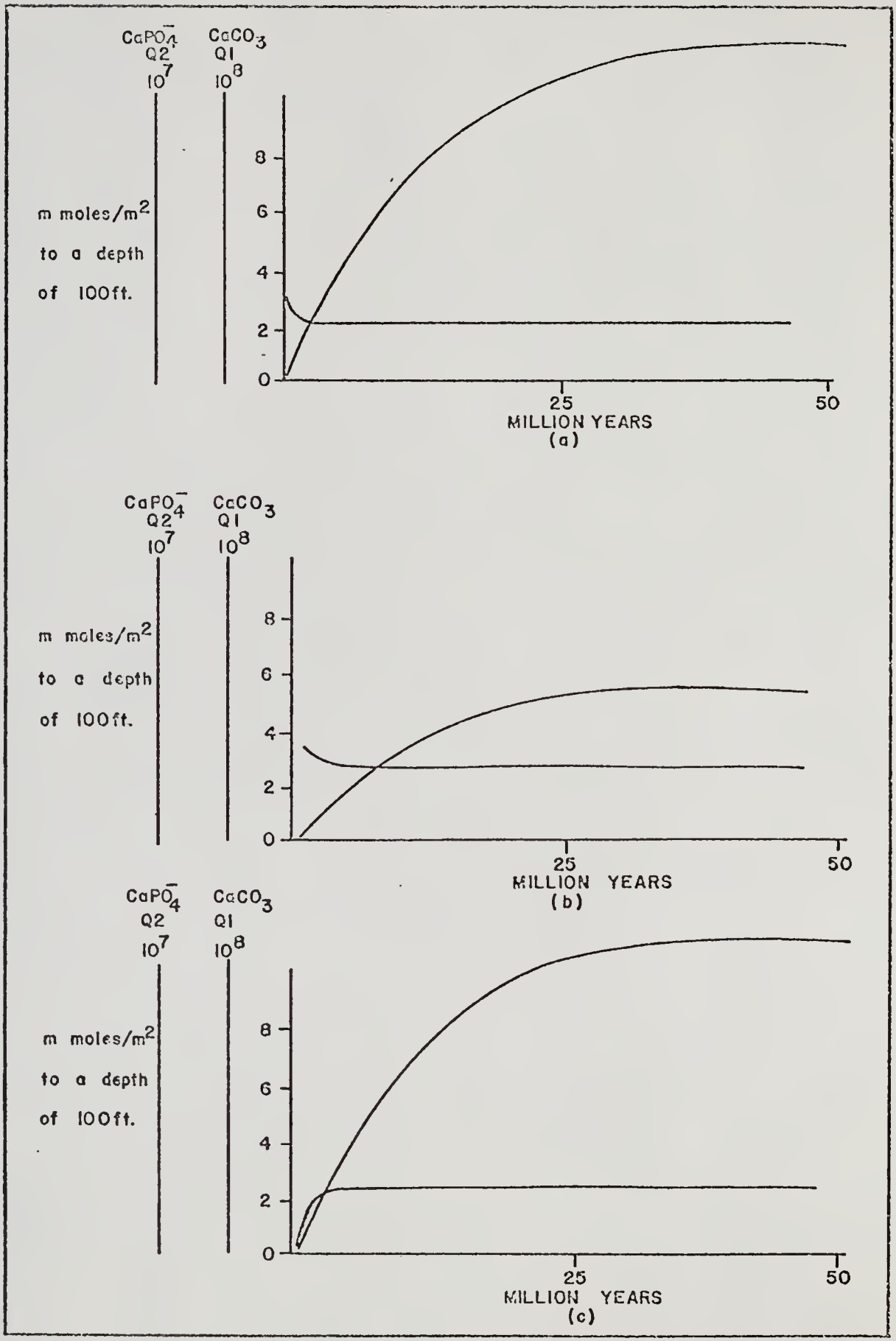
If the Miocene seas were unusually rich in phosphorus, the source of which may have been the upwelling of nutrients from deep in the ocean along the continental slope transported to Florida by lateral eddy diffusion, the ratio of $CaCO_3$ to $CaPO_4$ in new rock entering the system (J_3 and J_4) would be higher than in the original calculations where $CaPO_4$ was assumed to be .5 to 1% of the rock mass. A possible flux of phosphorus to Florida from the upwelling zone

Figure 41. Simulation of the geochemical deposition model in Fig. 38 for increased ratios of $CaPO_4$ to $CaCO_3$ in the estuarine material entering the system.

a. $CaPO_4$ content of the estuarine material is 5%; steady state content of Q_2 is 40%.

b. $CaPO_4$ content of the estuarine material is 1.7%; steady state content of Q_2 is 22%.

c. $CaPO_4$ content of the estuarine material is 3.4%; steady state content of Q_2 is 39%.


$CaPO_4^-$ Q2 10^7
$CaCO_3$ Q1 10^8
m moles/m² to a depth of 100ft.
0
2
4
6
8
25
50
MILLION YEARS
(a)
$CaPO_4^-$ Q2 10^7
$CaCO_3$ Q1 10^8
m moles/m² to a depth of 100ft.
0
2
4
6
8
25
50
MILLION YEARS
(b)
$CaPO_4^-$ Q2 10^7
$CaCO_3$ Q1 10^8
m moles/m² to a depth of 100ft.
0
2
4
6
8
25
50
MILLION YEARS
(c)

has been calculated (see discussion on phosphorus availability, page 157) to be 400 mg/m^2/year. When this "extra" elemental phosphorus was converted to $CaPO_4$ in sediment, it corresponded to 12.88 mmoles/m^2/year. Figures 41b and c depict the results of two simulation variations where J_4 was set equal to 5 and 10 mmoles/m^2/year. This corresponded to a $CaPO_4$ content of the new estuarine rock entering the system of 1.7% and 3.4% respectively. In the first case, the steady state concentration of $CaPO_4$ was 22% of the total rock mass and in the second case it was 39%. The $CaPO_4$ content of the Hawthorn formation ranges from 4 to 17% (Carr and Alverson, 1959).

MAN'S IMPACT ON THE PHOSPHORUS CYCLE OF FLORIDA

Energy Value of Phosphate Mining in Polk County (Fig. 42)

To complete the analysis of man and the phosphorus cycle in Florida, the energy budget of Polk County for the present condition (Table 9) and for the condition without the mining industry (Table 10) was calculated. Figure 42 gives the main energy and money flows in the county; Tables 9 and 10 describe the flows; and notes in Appendix A explain their derivation.

In regions under pressures of population increase, industrial development, or, as in this case, extensive mining operations, questions arise as to how best to use the land. What proportion of developed ecosystems to natural ecosystems maximizes the quality of life. Odum (1971) defined a theory of value based on the work done by the system where maximizing work values assures system survival. Odum and Odum (1972) proposed that quality of life is maximized when land uses are adjusted so that the sum of the value of natural ecosystems, developed ecosystems, and diversity interactions between the two is highest. In one model simulated in an environmental impact study of the Gordon River area near

Figure 42. Systems model of Polk County, Florida, showing the main energy and money flows.

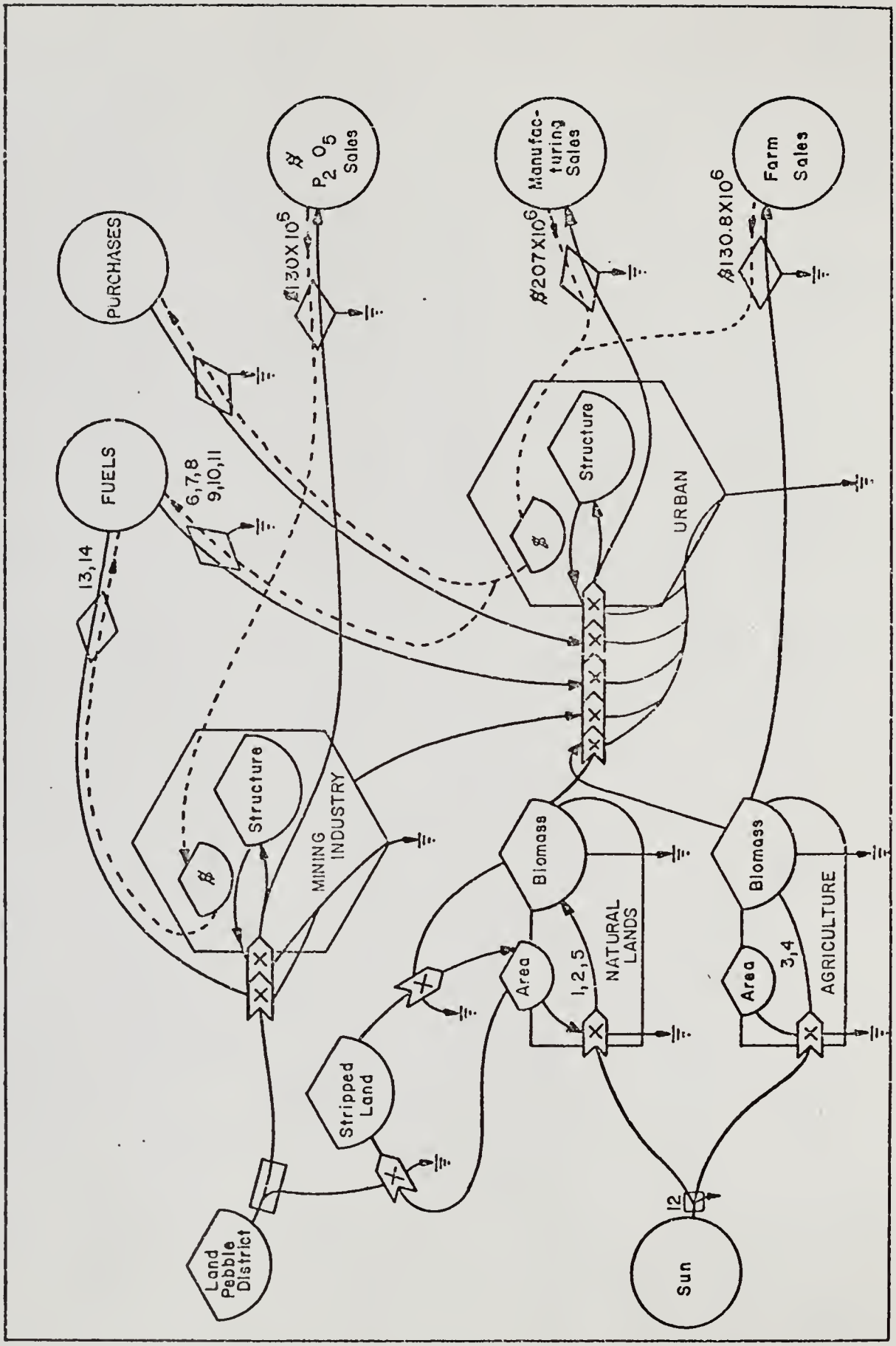

PURCHASES
FUELS
13,14
6,7,8
9,10,11
$ P2 O5 Sales
$130X10^5
Manufac-turing Sales
$207X10^6
Farm Sales
$130.8X10^6
Structure
MINING INDUSTRY
Structure
URBAN
Biomass
Area
1,2,5
NATURAL LANDS
Biomass
Area
3,4
AGRICULTURE
Stripped Land
Land Pebble District
12
Sun

Table 9

Energy Values in Polk County for the Present Condition

Pathway on Fig. 42	Name of Flow	Area[a] (acres)	Work[b] (kilocalx10^6/ acres/year)	Work for County[c] (kilocalx10^{11}/ year)	Dollar[d] Equivalent (million dollars/year)
	Undisturbed land				
1	Water	120,000[a]	32.8[f]	39.3	393
2	Pine flatwoods	36,000	60.0[g]	21.6	216
12	Heat gradients from the sun*				
	Nature's metabolic work on managed areas				
3	Pasture	875,400[a]	10.1[h]	88.4	884
4	Cropland	189,570[a]	21.4[i]	40.5	405
5	Stripped land	50,000[e]	5.0[j]	2.5	25
	Subtotal			192.3	1,923

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Table 9 (continued)

Pathway on Fig. 42	Name of Flow	Area[a] (acres)	Work[b] (kilocalx10^6/ acres/year)	Work for County[c] (kilocalx10^{11}/ year)	Dollar[d] Equivalent (million dollars/year)
	Urban				
6	Electricity			20.0[k]	200
7	Natural gas			23.9[l]	239
8	Kerosene			1.2[m]	12
9	Bottled gas			2.7[n]	27
10	Gasoline			34.0[o]	340
11	Food			2.0[p]	20
	Mining industry				
13	Natural gas			18.9[q]	189
14	Electricity**			21.0[r]	210
	Subtotal			123.7	1,237
	Total			316.0	3,160

*The heat gradients on land from the sun contribute to the natural work (e.g., microclimate); at present, the methodology for calculating this is unclear. Wind is also contributing work from the larger circulation of the atmosphere.

**Although electricity is a higher grade energy, it is added directly to the gas fuels since its concentration takes place outside the system.

Table 10

Energy Values in Polk County Without the Phosphate Mining Industry

Pathway on Fig. 42	Name of Flow	Area[a] (acres)	Work[b] (kilocalx10^6/ acres/year)	Work for County[c] (kilocalx10^{11}/ year)	Dollar[d] Equivalent (million dollars/year)
	Undisturbed land				
1	Water	120,000[a]	32.8[f]	39.3	393
2	Pine flatwoods	86,000[a]	60.0[g]	51.6	516
12	Heat gradients from the sun*				
	Nature's metabolic work on managed areas				
3	Pasture	875,400[a]	10.1[h]	88.4	884
4	Cropland	189,570	21.4[i]	40.5	405
	Subtotal			219.8	2,198

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Table 10 (continued)

Pathway on Fig. 42	Name of Flow	Area[a] (acres)	Work[b] (kilocalx10^6/ acres/year)	Work for County[c] (kilocalx10^{11}/ year)	Dollar[d] Equivalent (million dollars/year)
	Urban				
6	Electricity**			20.0[k]	200
7	Natural gas			23.9[l]	239
8	Kerosene			1.2[m]	12
9	Bottled gas			2.7[n]	27
10	Gasoline			34.0[o]	340
11	Food			2.0[p]	20
	Subtotal			83.8	838
	Total			303.6	3,036

*The heat gradients on land from the sun contribute to the natural work (e.g., microclimate); at present, the methodology for calculating this is unclear. Wind is also contributing work from the larger circulation of the atmosphere.

**Although electricity is a higher grade energy, it is added directly to the gas fuels since its concentration takes place outside the system.

Naples, Florida, Odum, Littlejohn, and Huber (1972) found that about 50% undeveloped and 50% developed ecosystems gave the highest regional value for that area. This distribution had higher total value than either the primitive condition or the fully developed condition. This is because the natural systems do not require maintenance by man, do not exert an economic load on the economy and, in fact, do work for man in providing waste control, water control, noise control, soil maintenance, microclimate, and recreation. Value calculations for a region often omit the work these natural systems do for the region. This is because we do not pay for nature's services with money. Value calculations which ignore nature's work obscure the true worth and costs within a system. Rather than the artificial dollar value, a natural measure of value is the energy budget of the system, whether it be urban or wilderness. The work of machines and people can be evaluated in some energy unit such as kilocalories. Similarly, a measure of the energy budget of a natural ecosystem is its gross primary productivity in kilocalories per acre per year (flow of chemical potential energy after sunlight is caught and concentrated). When these calculations are made, large energy values are found on land and in waters. By the theory, maximizing all energy contributions including those from natural systems will insure the long-range economic stability of a region. Present values for Polk County are given in Fig. 42.

In Polk County, as higher percentages of land are developed and strip mining denudes more land, natural areas may become in short supply. Their work contributions which were taken for granted may then have to be made up from the urban energy sector. This concern is manifested in the recent pilot scale attempts by the mining industry to reclaim wasted land so that it can again do its work for the county.

For present conditions in Polk County, the energy budget of the urban sector was 39% (Table 9) of the total budget (non-urban was 61%). The mining industry brings in fuels (urban energies) at the rate of 39.9×10^{11} kilocal/year (Table 9); however, losses in natural energies occur due to stripping the land at a current rate of 4,500 acres/year (Mr. Homer Hooks of the Florida Phosphate Council, personal communication). The loss due to the decreased productivity of the 50,000 acres previously stripped amounts to 27.5×10^{11} kilocal/year. For comparison, the energy budget of Polk County without the mining industry was calculated (Table 10); total energies were 303.6×10^{11} kilocal/year, of which 27.6% were urban. Total energies for the present conditions with mining were 316.0×10^{11} kilocal/year, which is 12.4×10^{11} kilocal/year higher than without mining. The implication is that Polk County is relatively undeveloped and the metabolic losses from the denuded land can be absorbed by the system, since there are extensive agricultural and natural areas. At the current rate of stripping land, however,

within five to ten years the total energies for the county without phosphate mining will be higher than with mining.

Effects on the Larger Systems of Phosphorus Mobilization Through Mining

Mobilization of phosphorus through mining not only affects the area where phosphorus is mined, but also the entire earth. As pointed out by Stumm (1972), the rate of mining of phosphorus exceeds the rate of transport to the sea, so that higher levels of phosphorus are being accumulated in a few percent of the earth's total land surface. For example, agriculture exerts a continual drain on the soil of phosphorus which is made up by the addition of phosphate fertilizers. The phosphorus from agricultural crops is found eventually in sewage which in turn is discharged to inland waters and estuaries. These changing rates of phosphorus cycling were evaluated here for the Peace River Estuary draining Florida's mining district and for Peninsular Florida.

Peace River Estuary

Based on observations and explained by simulation of the model in Figs. 9 and 10, the entire Peace River Estuary is high in total phosphorus ranging from .3 to 1.0 g/m^3 with the lower values in the southern sector of Charlotte Harbor. Since the river drains a basin with a soil and rock content uniquely high in phosphorus, the natural runoff

is the major phosphorus contributor. In the simulations neither daily mining water discharges nor sewage from present populations increased the phosphorus levels significantly. Phosphorus levels from sewage of a population 2-1/2 times larger than present showed little effect; the maximum change observed was during the dry season when a 16% increase in phosphorus in the river mouth occurred.

Simulation of a slime spill indicated that both short- and long-term changes were significant. Phosphorus concentrations increased drastically for several days and then leveled off higher than before the spill. Dry season levels were higher than levels during periods of maximum flow after a slime spill, whereas the inverse was true before a slime spill (Fig. 22). Phosphorus in the river mouth after a slime spill remained elevated for many years. High turbulence from a hurricane or greatly increased boat traffic caused erosion of the slime resulting in above normal turbidity in Charlotte Harbor.

Simulation of the model in Fig. 25 evaluated the effect of the high phosphorus levels on primary production in the estuary. The results indicated that the presence of high phosphorus keeps nitrogen levels low, possibly limiting productivity. At the present, primary production in this estuary is low relative to other Florida estuaries. The simulations indicated that productivity was quite sensitive to small increases in total dissolved nitrogen (Figs. 27,

28, and 29). When nitrogen input was increased to levels corresponding to secondarily treated sewage and urban runoff from a population of three to five times the present population, productivity increased to levels similar to the levels in Hillsborough Bay which suffers from frequent phytoplankton blooms and anaerobic bottom waters. Florida's population is still growing exponentially with the largest new growth expected on the southwestern coast. Much of the new development includes dredge and fill operations for finger canals, luxury housing, and condominiums. The simulation indicated that the wastes from this urbanization, if discharged into the estuary, may increase nitrogen concentrations, causing primary productivity increases to levels characterized by frequent phytoplankton blooms and anaerobic bottom waters.

Peninsular Florida

Florida is presently supplying three-fourths of the country's phosphorus needs (Florida Phosphate Council, 1973). Evaluation of the data for the peninsular Florida model (Fig. 33) indicated that Florida is draining its own rich supply 125 times faster than it is replaced. The new phosphorus sources created are dilute in comparison with the concentrated source of phosphate rock. The phosphorus extracted and thus mobilized by mining is higher by three orders of magnitude than the phosphorus cycling through Florida's waterways and than that brought in by rain. Of this enormous amount of phosphorus mobilized by mining,

.9% of that marketed is used in agriculture in Florida (60% in the United States), increasing the flux between land and waterways in Florida by one and one-half times. Forty percent of the phosphorus mined stays in Florida in the form of slime and other waste products.

Sewage and agricultural runoff may contribute to an increase of phosphorus in Florida's inland waters. Total input to inland waters is 133 mg/m^2/year of which 78 mg/m^2/year (Fig. 33) or 58.6% is a result of man's activities. The 78 mg/m^2/year includes urban runoff, sewage effluent, agricultural runoff, and mining effluent. Of these, the largest contributor is agriculture with 58 mg/m^2/year in runoff or 34% of the total input to inland waters. Sewage effluent to inland water is a minor contributor (7.4 mg/m^2/year). Since a large proportion of Florida's population resides in coastal cities, a large proportion of the total sewage is discharged into estuaries. Sewage effluent contributes 30 mg/m^2/year phosphorus to the estuaries,a small amount compared to the large quantities brought in by the enormous quantities of water involved in tides. Where estuarine conditions are such that tidal flushing occurs readily, phosphorus from land sources may not be significant. On the other hand, in enclosed or protected estuaries where little tidal input occurs, sewage effluent may be an important contributor of phosphorus to the estuary.

New Phosphorus Storages

Lakes and estuaries may be trapping and storing nutrients. The ratio of phosphorus in lake and estuarine water to that in lake and estuarine sediments is 1 to 1,000 (Fig. 33), indicating that the sediment is acting somewhat like a sink for phosphorus. Lakes may be viewed as large soil solution spaces and thus may function in similar ways in concentrating phosphorus. The lake, then, is part of the overall geochemical process discussed earlier of dissolution and reprecipitation of calcium phosphate at the expense of calcium carbonate. Phosphorus concentrations in the sediment of Charlotte Harbor and Hillsborough Bay which receive the drainage from the mining district is higher by one and one-half orders of magnitude than other Florida estuaries averaging 2,800 g/m^3. Phosphate rock averages 80,600 g/m^3 phosphorus (Bureau of Mines, 1969); an increase over these estuaries of only 28 times. As estuarine sediment becomes sedimentary rock, the compaction and resulting increase in density may increase the relative phosphorus concentration further. As this sediment becomes land, further phosphorus enrichment by percolating water, as postulated previously, may occur, resulting in a relatively high grade phosphate rock.

Sedimentation Rates

If the rate of phosphorus loss to sediment is assumed indicative of sedimentation rates for lakes and estuaries,

the upper five feet have accumulated in one to three thousand years (Fig. 33). Assuming two thousand years results in a sedimentation rate of 2.5 feet/1,000 years or .76 m/1,000 years. Rusnak (1967) in his article on rates of sedimentation in modern estuaries stated that a rate of 5'/1,000 years or 1.5 m/1,000 years was a good estimate for estuaries that remain at steady state with the present sea level fluctuations. It may be fortuitous that this is the same rate for estuaries alone (excluding lakes) found in this study, that is, 5'/1,000 years. If isostatic adjustments in Florida keep pace with erosion, then an estimate of the present uplift rate is possible. If 1.5 meters of sediment have accumulated in 1,000 years over all the estuarine area considered in this study or 4.9×10^9 m^2, a total volume of 7.35×10^9 m^3 of sediment has been eroded from Florida. The area of Florida considered here is 10^{11} m^2, implying a loss from the peninsula of .07 meters/1,000 years. If isostatic adjustment is keeping pace, then Florida is also rising at .07 m/1,000 years.

Implications for Phosphorus Management in Florida

Two concerns with changes in phosphorus cycling rates are apparent. First,will the economic world run out of phosphorus and second, is there excessive enrichment of phosphorus in inland waters due to increased mobilization of the element from mining. At present rates of extraction, there is a 50-year reserve of high grade phosphate rock in

Florida (Fig. 35). Florida's supply could be greatly extended if the loss in washer and flotation processes which is now about 40% of the phosphorus in the land pebble fields (U.S. Bureau of Mines, 1970) was diminished. However, the energy costs of this may exceed its worth. More judicious and efficient use of phosphate fertilizers on agricultural land would serve a dual purpose in conserving phosphorus (60% of Florida's production goes into agriculture in the United States) and in decreasing the phosphorus content of agricultural runoff to inland waterways. Phosphorus use in detergents and food in peninsular Florida is 18.5% of that used in agriculture (68.6 mg/m^2/year vs 370 mg/m^2/year from Fig. 33). In certain local situations where a relatively large quantity of effluent is discharged into a small lake, sewage is undoubtedly a significant contributor; however, since most Floridians live in coastal cities, sewage effluent may not be implicated on a statewide basis as a large contributor to inland waters.

Genesis of Phosphate Rock

Consider the concept of uniformitarianism often stated "the present is the key to the past." Are present processes adequate to account for Florida's geochemical phosphorus concentrations? Present ionic concentrations of Ca^{++}, HCO_3^-, and $HPO_4^=$ in surface waters versus groundwaters in Florida indicate that phosphorus can become concentrated in rock through dissolution and reprecipitation. Specifically,

Ca^{++} and HCO_3^- ionic concentrations increase with percolation whereas $HPO_4^=$ concentrations decrease (Table 7). Simulations of the model in Fig. 38 examined the degree of concentration possible under various conditions and the time it takes to achieve some level. The results indicated that, if there is any phosphorus at all in the original land mass or in the original sediment becoming land, phosphates will concentrate to some extent with steady state levels being reached in twenty-five million years (Fig. 39). If the content of original rock and new sediment is 1% $CaPO_4$ by weight, then the steady state rock content after twenty-five million years is 14.5% (Figs. 39a and b); if the original rock is 0.5% $CaPO_4$, then the steady state content is 10% (Fig. 39c). Indications are that, with the present phosphorus content of rain, dissolution and reprecipitation by downward percolating ions coupled with uplift, where the original rock being dissolved and the new rock entering the system are relatively pure limestones such as the Ocala and Suwannee, will yield a Hawthorn type $CaPO_4$ content (4 to 17% from Carr and Alverson, 1959). Furthermore, the simulations indicated that this same process acting on the Hawthorn formation could result in phosphate concentrations as high as those in the Bone Valley and Alachua formations. Specifically, the simulation variations (Figs. 41a, b, and c) in which the rock entering the system was given a $CaPO_4$ content of 1.7%, 3.4%, and 5% (the Hawthorn formation

averages 5%) yielded steady state $CaPO_4$ contents of 22%, 39%, and 40% respectively. The Bone Valley formation averages 31% $CaPO_4$.

Since numerous authors have called on special circumstances such as nutrient upwelling in the ocean and bird guano deposits to account for the phosphorus in sedimentary phosphate rock, the model was tested for these conditions.

Based on a hypothetical source of phosphorus along the continental slope in the Gulf of Mexico, calculations indicated that lateral eddy diffusion could readily transport to the present Florida land mass 400 mg of phosphorus per meter squared of Florida per year. If precipitated and assuming a typical sedimentation rate of .03 m/1,000 years, a phosphorus flux of 450 mg P/m^2/year (1950 mg $CaPO_4/m^2$/year) is required to form a sediment with a Hawthorn type $CaPO_4$ content (5% average).

If bird rookeries are called on to account for the Hawthorn phosphates, the source of phosphorus must still be outside the system; that is, some movement of phosphorus from the sea must occur to supply the fish food chain. Some guano may then be dissolved by rain and returned to the ocean, but annual phosphorus uptake by birds can not be greater than the influx to the birds' food supply from the sea.

In summary, the geochemical conditions presently observed (excluding man's changes), if extended over tens of millions of years, are sufficient to account for Florida's

phosphates. Nutrient upwelling, although it may have occurred, is not required. The original phosphorus deposited in the sea with the Eocene limestones or with the Miocene Hawthorn formation may have been quite small. As sea levels fluctuated, the formations were exposed to percolation of groundwater downward. The calcium phosphate, then, became greatly enriched, with the original particles acting as the nucleating surfaces. With the Hawthorn phosphates as a source, the Bone Valley and Alachua phosphates were further enriched by the same process.

Suggestions Pertinent to Pollution Regulations and Resource Management

The systems models used to measure the impact of man on phosphorus flows indicated the following:

1. Since phosphorus levels are naturally high in the Peace River and Charlotte Harbor, requiring advanced waste treatment for phosphorus removal from domestic sewage or from the daily mining effluent discharged to the river may not have any advantages.

2. Since slime spills were deleterious to the Peace River and Charlotte Harbor both in the short and long terms, the strict controls and monitoring of the earthen dams recently begun by the state of Florida is warranted.

3. The simulation indicated that increased urbanization of the area with associated increased nitrogen discharges

to the system (from sewage, urban runoff, finger canal construction, and agriculture) may increase primary productivity in Charlotte Harbor, but not to levels common in other normal Florida estuaries. If sewage discharges to the estuary increase to five times the present, discharge to terrestrial systems or nitrogen removal should be considered.

4. Since, in Florida, agricultural runoff from fertilized cropland is the highest man-dominated phosphorus flow to inland waters, more judicious and efficient use of phosphate fertilizers is warranted.

5. Phosphorus in domestic sewage from detergents and food may not be implicated on a statewide basis as a large contributor to inland waters. Although certain local situations may call for it, banning phosphate detergents on a statewide basis is not warranted.

6. When United States phosphorus reserves become depleted, the enormous quantities of phosphate stored in the mine tailings and slime ponds in Florida may be looked to as a phosphorus source. In preparation for this, an energy cost-benefit study of the energy cost of obtaining the phosphorus versus the energy benefits the phosphorus produces at its point of use (e.g., value of fertilized crops) should be evaluated.

7. At the present, the work done for Polk County by the phosphate industry slightly increases the total work done or power output of the county. As more land is required,

however, the work losses to the system from denuding this land may exceed the work done by phosphate mining. Schemes for quickly recovering the land after stripping should be examined.

The research generated several principles which may have general scientific value. First, the presence of high phosphorus levels in Charlotte Harbor kept nitrogen levels low and primary productivity was low. The question then arises, could the extreme excess of one nutrient make an aquatic system more oligotrophic? If so, this is somewhat countercurrent to intuition. Second, water quality control programs based on the percent effect of a given flow on the overall chemical cycle may be more meaningful and efficient than the current practice of setting effluent standards based on concentrations. Third, the ocean may be considered as a source of phosphorus to the land through rain or estuarine sediment. The phosphorus in estuarine sediment is obtained from the oceanic waters by marine organisms such as clams and fish or by birds through guano deposits. The amount available depends on the oceanic transport to the estuary. Later, uplift of the estuarine sediment may concentrate the phosphorus.

APPENDIX A

NOTES TO TABLES 3, 5, 6, 8, 9, AND 10

Notes to Table 3

1. Calculated in note 19 of Table 6.
2. A pond with a capacity at least as large as that required for the Cities Service slime spill of 1971 is required; this is 30×10^6 m^3 (Harriss et al., 1972) and corresponds to the full condition or the threshold (R_1).
3. Toler (1967) gives the phosphorus concentration in the slime holding ponds as 7,540 mg/l or 7,540 g/m^3.
4. Referring to the U.S. Coast and Geodetic Survey Map and Alberts et al. (1970), the salt water line is slightly north of Liverpool. The area included as river mouth begins on the north at the bridge on State Road 761, which crosses the river at latitude 27°05'20" and extends south to Bascule Bridge, crossing the river at the town of Charlotte Harbor and Punta Gorda at latitude 26°57'. Not considering marsh, the area of water is 3.02 sq. naut. miles from the northern boundary south to Bird and Coon Keys. Average depth here at mean low tide is six feet (3.7×10^7 ft^2/naut. mile x 3.02 naut. miles = 11.17×10^7 ft^2 x 6' deep = 67.02×10^7 ft^3 = 1.897×10^{10} liters). The area from Bascule Bridge north to Bird and Coon Keys is 76.5×10^8 liters (270×10^7 ft^3 or 90×10^6 ft^2 x 3' deep); 1.897×10^{10} liters plus $.765 \times 10^{10}$ liters = 2.662×10^{10} liters or 2.662×10^7 m^3. Total surface area (A_4) is 11.17×10^7 ft^2 + 9×10^7 ft^2 = 19.17×10^7 ft^2 = 1.78×10^7 m^2. Average

depth is 94.02×10^7 ft^3/19.17×10^7 ft^2 = 4.904 feet = 1.49 meters. The bottom of the river mouth is 1.9 meters above the bottom of Charlotte Harbor; this is Z in the model.

5. Alberts et al. (1970) give the dissolved phosphorus concentration of the Peace River Mouth as .6 mg/l in March, .57 mg/l in December, and .53 mg/l in August. An initial condition of .6 mg/l was chosen, yielding .6 mg/l x 2.662×10^{10} liters = 1.597×10^{10} mg phosphorus or 1.597×10^7 g.

6. From the U.S. Coast and Geodetic Survey Map the area is defined on the northern end at Bascule Bridge on the Peace River and at Cattle Dock on the Myakka River. It extends south to Cape Haze at latitude 26°45'25". The area (A_6) is $1{,}580.87 \times 10^6$ ft^2 = 1.468×10^8 m^2 at a depth at mean low tide of 10.45 feet, yielding a volume of $16{,}517.84 \times 10^6$ ft^3 or 4.67×10^{11} liters = 4.67×10^8 m^3.

7. Alberts et al. (1970) give the dissolved phosphorus concentration of the northern part of Charlotte Harbor as .35 mg/l. Volume is 4.67×10^{11} liters so that total phosphorus is 4.67×10^{11} liters x .35 mg/l = 1.63×10^8 g.

8. From the U.S. Coast and Geodetic Survey Map the area is defined on the northern end at Cape Haze, latitude 26°45'25", and on the southern end by the 6' contour line at the north edge of Pine Island, latitude 26°40'30".

Surface area (A_8) is $2{,}013.97 \times 10^6$ ft^2 = 1.871×10^8 m^2 at an average depth at mean low water of 9.5 feet, yielding a volume of $19{,}132.7 \times 10^6$ ft^3 = 1.9133×10^{10} ft^3 = 5.38×10^{11} liters = 5.38×10^8 m^3.

9. Alberts et al. (1970) give the dissolved phosphorus concentration of the southern part of Charlotte Harbor as .31 mg/1 in August, .15 mg/1 in December, and .12 mg/1 in March. A value of .25 mg/1 was chosen as the initial condition so that phosphorus is 5.38×10^{11} liters x .25 mg/1 = 1.34×10^{11} mg = 1.34×10^8 g.

10. Huang and Goodell (1967) show that the PO_4 content in the sediment at the lower river mouth (Bascule Bridge) is 1 to 2% and is .4% six miles upstream with an average thickness of recent sediments of 10 feet. The area here is 1.917×10^8 ft^2 (note 4). Volume of sediment assuming just the upper one foot as important is 1.917×10^8 ft^3 x 1% PO_4 = 1.917×10^6 ft^3 PO_4 x 1/3 = $.6 \times 10^6$ ft^3 P x 28,320 cc/ft^3 x 1.82 g/cc = $.6 \times 10^6$ ft^3 P x 5.15×10^4 g/ft^3 = 3.09×10^{10} g P/1.9×10^8 ft^3 = 151 g/ft^3. Considering only the active portion of sediment or the top six inches (Pomeroy, 1972), this is 75 g/ft^3 six inches deep or 883 g/m^2 six inches deep; 883 g/m^2 x 1.78×10^7 m^2 = $1{,}572 \times 10^{10}$ g.

For comparison, consider the values in Harriss et al. (1972). They state that there is .74 to 1.7 ppt total phosphorus in the lower river mouth sediments (1.2 ppt

$= 1.2 \times 10^{-3} \times 5.15 \times 10^{4}$ g/ft^3 = 61.8 g/ft^3). In the upper part of the estuary, around the salt water line total phosphorus is 2.4 ppt before a slime spill and 13 ppt after a spill; 2.4 ppt corresponds to 123.6 g/ft^3 and 13 ppt corresponds to 615 g/ft^3.

11. Huang and Goodell (1967) show that PO_4 is 3% in the sediments or .01 P x 28,320 cc/ft^3 x 1.82 g/cc = 515 g P/ft^3 = 2,941 g/m^2 considering the top six inches; 2,941 g/m^2 x 1.468×10^{8} m^2 = 4.3×10^{11} g.

12. Same as number 11, but multiplied by this area: 2,941 g/m^2 x 1.871×10^{8} m^2 = 5.5×10^{11} g.

13. Capacity of sewage treatment plants whose effluent goes into the Peace River as given by the Inventory of Sewerage Systems in Florida (1966) and in the EPA Publication Municipal Waste Facilities 1968 Inventory.

Auburndale	.6 MGD
Bartow	2.75
Cypress Gardens	.036
Fort Meade	.35
Lake Alfred	.3
Lakeland	9.0
Lake Wales	1.0
Winter Haven	3.0
Wauchula	1.0
Arcadia	.65
2 Hospitals	.315
Harbour Heights	.0322
Port Charlotte	.68
Punta Gorda	.210
	19.9232 MGD = 75.4×10^{3} m^3/day

14. The phosphorus content of the sewage entering the river is 5 mg/l or 5 g/m^3. (This is average concentration of phosphorus in sewage after secondary treatment, from Am. Chemical Society, 1969.)

15. Lanquist (1953), quoting the Florida State Board of Health, says that 60% of the Peace River flow at Ft. Meade is from mining effluent upstream. At an average river flow of 920 cfs (Specht, 1950) this is 552 cfs from mining or 1.33×10^9 liters/day or 1.33×10^6 m^3/day.

    To verify this value, Specht states that 10% of the clear effluent from the slime ponds is not reused but is wasted to the river. Water use in the industry is about 3.8×10^9 gal/day (Stewart, 1966). Ten percent of this is 3.8×10^9 gal/day; assuming about half of this is associated with mining in the Alafai River Basin, this leaves 1.9×10^9 gal/day x 3.78 l/gal = 7.182×10^9 l/day or 7.182×10^6 m^3/day. From two sources results are 1.33×10^6 m^3/day and 7.182×10^6 m^3/day. The lower value is chosen, 1.33×10^6 m^3/day.

16. Specht (1950), in an example pond, states that it takes 1-1/2 years to accumulate 6.5×10^6 gallons to fill an average pond. The average pond used here is large (note 2), so assume it takes two years to fill it or 30×10^6 m^3/720 days = 41,700 m^3/day.

17. Specht (1950) states that a rainfall of about seven inches in one day is required for a major dam break.

18. Primary river flow is given for 1964 by Dragovich et al. (1968) and for 1961-1968 by the U.S. Geological Survey. From this was derived a sin wave with a frequency of 2 radians per year with maximum flow in August and

September and minimum flow in February and March. The sinewave is adjusted in the computer program so that low flow corresponds to 0.1×10^6 m^3/day; intermediate flow corresponds to 5×10^6 m^3/day; and maximum flow corresponds to 10×10^6 m^3/day.

19. The U.S. Geol. Survey (1961-1968) gave PO_4 concentrations for the Peace River and for tributaries not receiving wastes. Although their data are quite variable with concentrations ranging from .8 mg/l to 5.9 mg/l as P, an average of 1.5 mg/l was calculated.

20. Dragovich et al. (1968) gave the Myakka River discharge for each month. The yearly average was 5×10^5 m^3/day.

21. Total phosphorus for the Myakka River was given in Dragovich et al. (1968) as ranging from .301 to .465 mg/l.

22. This can be any factor that might cause phosphate deposition in the sediment; examples are increased pH and increased available nitrogen. As a measure of this pathway, the total N concentration was used. The U.S. Geological Survey (1961-1968) gives an average of .15 g/m^3.

23. Turbulence in kilocalories/day = potential energy of a tide x distance it moves.

P.E. = $mg\Delta h$;

M = mass of water in the tide;

density of sea water = 1.024 g/cc = 1.024×10^3 kg/m^3;

volume of water in tidal prism affecting river mouth
$= 1.78 \times 10^7 \text{ m}^2 \times .3 \text{ m} = .534 \times 10^7 \text{ m}^3$;
$.534 \times 10^7 \text{ m}^3 \times 1.024 \times 10^3 \text{ kg/m}^3 = .547 \times 10^{10}$ kg;
$g = 9.8 \text{ m/s}^2$;
h = 1 foot = .3 m
P.E. = $(.547 \times 10^{10} \text{ kg})(9.8 \text{ m/s}^2)(.3 \text{ m}) = 1.6 \times 10^{10}$ Newtons;
Power = N.m = joules.
This P.E. is exerted over a distance of 16,000 yds.
or 14,630 m.
Power = $(1.6 \times 10^{10} \text{ N})(14{,}630 \text{ m}) = 23.4 \times 10^{13}$ joules;
23.4×10^{13} joules $\times 2.389 \times 10^{-4}$ kilocal/joule
$= 56.16 \times 10^9$ kilocal/day.

24. Same as note 22 except .018 g/m^3 (Alberts et al., 1970).

25. Volume of water = $1.468 \times 10^8 \text{ m}^2 \times (1.7 \times .3) \text{ m}$
$= (1.468 \times 10^8 \text{ m}^2)(.51 \text{ m}) = .734 \times 10^8 \text{ m}^3$;
$1.024 \times 10^3 \text{ kg/m}^3 \times .734 \times 10^8 \text{ m}^3$
$= .75 \times 10^{11}$ kg.
As in note 23, P.E. = $(.75 \times 10^{11} \text{ kg})(9.8 \text{ m/s}^2)(.51 \text{ m})$
$= 3.7 \times 10^{11}$ N;
Joules = $(3.7 \times 10^{11} \text{ N})(12{,}000 \text{ yds.} \times .9144 \text{ m/yd})$
$= (3.7)(10.8) \times 10^{14}$ joules $= 39.96 \times 10^{14}$ joules;
39.96×10^{14} joules $\times 2.389 \times 10^{-4}$ kilocal/joule
$= 95.76 \times 10^{10}$ kilocal/day.

26. Same as note 24.

27. Vol. of water = 1.871×10^8 m^2 x .5/m = $.935 \times 10^8$ m^3 x 1.024×10^3 kg/m^3 = $.957 \times 10^{11}$ kg.
P.E. = $(.957 \times 10^{11}$ kg$)(9.8$ m/$s^2)(.51$ m) = 4.75×10^{11} N; 4.75×10^{11} N exerted over a distance of 16,000 yds or 14,640 m.
Power = $(4.75 \times 10^{11}$ N$)(14.63 \times 10^3$ m) = 69.5×10^{14} joules; 69.5×10^{14} J x 2.389×10^{-4} kilocal/J = 166.5×10^{10} kilocal/day.

28. The mean tidal range for Charlotte Harbor is 2.6 feet with one high tide and one low tide per day. A function corresponding to a sin wave with an amplitude of 1.3 feet and a frequency of 2π radians per day is entered in the model.

29. Phosphorus content of the sea water outside the harbor is given by Graham (1954) as .031 mg/l or .031 g/m^3.

30. Due to the large amount of phosphorus in Q_1, Q_1 is considered as an infinite source or a forcing function and, thus, the flow out of it is constant. Toler (1967) gives the phosphorus concentration of the slime holding ponds as 7,540 g/m^3.

31. Lanquist (1953) states that the phosphorus concentration in mining water wasted to the river is 1 g/m^3.

32. From note 2, the water released from the pond is slightly less than 30×10^6 m^3. Assuming it is released all in one day yields a flux of 28.8×10^6 m^3/day. The flow stops when the quantity of water in Q_2 goes below the threshold value R_A chosen as 1.0×10^4 m^3.

33. The phosphorus released to the Peace River when the dam breaks is the concentration 7,540 g/m^3 x 28.8×10^6 m^3/day or 2.1715×10^{11} g/day.

34. At low tide and river low flow, which represents the initial condition of the model, the flow out of the river mouth is simply the river discharge or $.1 \times 10^6$ m^3/day (footnote 18). The tide brings in and out 19×10^7 ft^3 of water (19×10^7 ft^2 from note 4 of area x 1' depth, U.S. Dept. of Commerce, 1972). This is about 2×10^8 ft^3/day or 5.665×10^6 m^3 of water in and out each day plus $.1 \times 10^6$ m^3 = 5.765×10^6 m^3 of water.

35. When the river load exceeds its capacity, which corresponds to a phosphorus concentration of 8 g/m^3 (R2), something which occurs principally during a slime spill, phosphorus is deposited directly by gravity settling in the river mouth. Harriss et al. (1972) state that the Cities Service Spill blanketed the Upper Peace River Estuary with an average of 3" of slime and a maximum of 6" of slime. Slime is 30% P (Harriss et al., 1972) and the area is 1.917×10^8 ft^2 x 3/12 ft deep = $.479 \times 10^8$ ft^3 slime x 30% = $.14 \times 10^8$ ft^3 P x 5.15×10^4 g/ft^3 = 7×10^{11} g P deposited. The slime spill chosen will release 2.17×10^{11} g P.

36. Huang and Goodell state that there has been no overall erosion or deposition in the area over the last 100 years so that a steady state condition between deposition

of particulate P from biological processes and redissolving it from turbulence is assumed. Harriss et al. (1972) give the rate of phosphorus being dissolved from sediment into the surface water after a slime spill. Take 1/3 of this as a first approximation to the steady state condition. Harriss states that 375 ppm of the slime is P which is soluble and that for the Cities Service Spill, this phosphorus will be an input to the river for 2 to 10 years. I have assumed the intermediate value of 6 years here. The average of 3" of slime over 1 sq ft - 1/4 ft^3 slime x $375x10^6$ soluble P = $94x10^6$ ft^3 P/ft^2 area available; $94x10^{-6}$ ft^3 x 28,320 cc/ft^3 x 1.82 g/cc = 4.8 grams P/ft^2 area available. Average depth is 5' = 5 ft^3 of water or 141.6 l of water above the 4.8 g/ft^2 available over a six-year period = $\frac{4,800 \text{ mg}}{141.6 \times 2,190 \text{ days}}$ = .0155 mg P/l/day x $2.66x10^{10}$ l = $4x10^8$ mg/day. Take 1/3 of this for the steady state condition to give $1.33x10^8$ mg/day or $1.33x10^5$ g/day. To verify this number, Pomeroy et al. (1972) give values ranging from 8 to 14 mg P/m^2/day as the exchange rates for three shallow turbid estuaries on the Georgia coast. Assuming 10 or .01 g/m^2/day x $1.78x10^7$ m^2 = $1.78x10^5$ g/day slightly higher than the value of $1.3x10^5$ g/day derived above. The higher value is expected due to the very turbid nature of the estuary.

37. Since steady state is assumed, the value is the same as that derived in footnote 36 -- $1.33x10^5$ g/day.

38. Concentration of phosphorus is .6 mg/l (note 5) and the flow at low tide and river low flow is 5.76×10^6 m^3/day (note 34), yielding 3.456×10^6 g/day as the phosphorus flux out of the river mouth.

39. Into the Peace River mouth on a flood tide comes 5.66×10^7 m^3/day (note 34) at a concentration of .35 g/m^3 (note 7), yielding a phosphorus flux of 1.98×10^6 g/day.

40. From the U.S. Dept. of Commerce (1972), the flux of water in and out with tide changes the elevation by 1.9' over an area of $1,581 \times 10^6$ ft^2 or $3,004 \times 10^6$ ft^3 of water are brought in and out with the tide. This is 8.5×10^{10} liters per half day in and out or 8.5×10^7 m^3/day.

41. The flux of phosphorus out of the harbor area on an ebb tide is 85×10^6 m^3/day (note 40) x .35 g/m^3 (note 7) = 2.975×10^7 g/day.

42. The rate calculated is .0155 mg P/1/day x 1/3 (note 36) x 4.67×10^{11} 1 of water = 2.4×10^6 g/day. Pomeroy's estimate discussed in note 36 yields .01 g/m^2/day x 1.468×10^8 m^2 = 1.468×10^6 g/day, which is close to the value above.

43. Since steady state is assumed, it is the same as that derived in note 42 == 2.4×10^6 g/day.

44. The flux of phosphorus into the harbor on a flood tide is 8.5×10^7 m^3/day (note 40) x .25 g/m (note 9) = 2.12×10^7 g/day.

45. The flux of water in and out of the lower harbor through Boca Grande Pass with the tide can be obtained using the O'Brien equation derived for sandy inlets. $P = 5x10^4 A$ where A is the cross-sectional area of the smallest part of the inlet in ft^2 (width x depth) and P is the tidal prism in ft^3. The smallest cross-sectional area is 81,000 ft^2, therefore $P = (5x10^4)(81x10^3) = 4.05x10^9$ ft^3 in and out with the tidal cycle or $1.13x10^8$ m^3 in and out /day.

46. The flux of phosphorus into the lower harbor from the sea with the incoming tide is $1.13x10^8$ m^3/day (note 45) x .031 g/m^3 (note 29) = $3.5x10^6$ g/day.

47. The flux of phosphorus out of the lower harbor is $1.13x10^8$ m^3/day (note 45) x .25 g/m^3 (note 9) = $2.825x10^7$ g/day.

48. Assuming a steady state and the value of .0155 mg P/l/day x 1/3 obtained in note 36, $5.38x10^{11}$ l x .00517 mg/l/day = $2.78x10^6$ g/day.

49. Since steady state is assumed, the value is the same as that derived in note 48 -- $2.78x10^6$ g/day.

Notes to Table 5

1. Total dissolved nitrogen is given by Connell and Associates (1972) as .1 mg/1. Finucane and Dragovich (1959) give .2 mg/1. The intermediate or .15 mg/1 is used. The computer simulation predicts an average water volume of 50×10^6 m^3 so that total nitrogen is 50×10^6 m^3 x .15 g/m^3 = 7.5×10^6 g.
2. An average phosphorus concentration for the river mouth of 1.0 g/m^3 is chosen based on data from Dequine (personal communication), Alberts et al. (1970), and on the concentration predicted by the computer simulation. Volume of water is 50×10^6 m^3 so that total phosphorus in the water is 1.0 g/m^3 x 50×10^6 m^3 or 50×10^6 g P.
3. Incoming radiation varies seasonally from 2,000 kcal/m^2/day to 5,500 kcal/m^2/day with an average value of 3,800 kcal/m^2/day (E. P. Odum, 1971). About 50% of incoming radiation is used in photosynthesis (H. T. Odum, 1971) or 1,900 kcal/m^2/day for the average. The surface area of the estuary is 1.78×10^7 m^2 (note 4 of Table 3). Light captured is 1,900 kcal/m^2/day x 1.78×10^7 m^2 or 3.38×10^{10} kcal.
4. Spence (1971) did cell counts for the Charlotte Harbor area. She found an average of 5.34×10^5 cells/liter. Some cell sizes were given (Cyclotella species) and an average size of 20u diameter and 5u depth was chosen

in order to calculate standing crop in g/m^3. The above cell dimensions yield a volume of 1,600 u^3 = $1,600 \times 10^{-12}$ cm^3 multiplied by the total number of cells (5.34×10^5 cells/liter) equals 8.5×10^{-4} cm^3/liter or .85 cm^3/m^3. Assuming the plankton have the same density as water, this yields a concentration of .85 g/m^3. Total standing crop is then .85 g/m^3 x 50.0×10^6 m^3 = 42.7×10^6 g.

5. The average incoming solar radiation for this latitude is 4,800 kcal/m^2/day (Odum, 1971) over an area of 1.78×10^7 m^2 = 6.76×10^{10} kcal/day.

6. Lanquist (1953) gives turbidity values for the Peace River. An average value for the river mouth if 10 ppm.

7. The U.S. Geol. Survey (1961-1968) gives nitrate concentrations in the Peace River at Arcadia, Florida (13 miles upriver from the mouth), corresponding to .154 g/m^3 N. Total nitrogen is undoubtedly higher. Odum et al. (1955) give a 1952 Kjeldahl nitrogen value of .336 g/m^3. Total nitrogen is given a starting value here of .47 g/m^3. The average river flow calculated from the USGS data and predicted by the computer simulation is 6.3×10^6 m^3/day. This yields a nitrogen flux of 3.0×10^6 g/day.

8. The average phosphorus input from upstream calculated for the large estuarine system (notes 13,14,15,18, 19, and 31 of Table 3) is 7.6×10^6 g/day, corresponding to an incoming concentration of 1.2 g/m^3.

9. An estimate of the daily flux of phosphorus from surface waters to sediment as calculated in note 36 of Table 3 is $.133 \times 10^6$ g/day.

10. The phosphorus exported downstream is the phosphorus concentration in the river mouth (note 2 of this table) multiplied by the amount of water discharged (footnote 7 of this table) or 1.0 g/m^3 x 6.3×10^6 m^3/day = 6.3×10^6 g/day.

11. The quantity of phosphorus daily incorporated into phytoplankton biomass depends on the production of the area. Although no productivity studies have been done for this area, Harriss et al. (1972), Spence (1971), and Connell and Associates (1972) all state that productivity in Charlotte Harbor is one of the lowest in South Florida. If it is assumed that the turnover time for phytoplankton is once a day, then productivity equals standing crop or 42.7×10^6 g (note 4 of this table) or .85 g org. matter/m^3/day = .85 g O_2/m^3/day. To convert grams of oxygen to grams phosphorus involved in the productivity, consider the ratio given in Sverdrup (1942, p. 237) of O:C:N:P = 109:41:7.2:1. The production here is .85 g/m^3/day, yielding a ratio of .85/54.5 (109÷2) equals .015. The phosphorus involved in the productivity, then, is 1x.015 = .015 g P/m^3/day. Multiplying by the volume of water (50×10^6 m^3) yields $.75 \times 10^6$ g P/day.

12. The nitrogen exported downstream is the nitrogen concentration in the river mouth (note 1 of this table) or 0.15 g/m^3 x 6.3×10^6 m^3/day equal to 0.95×10^6 g/day.

13. From note 11 of this table it was calculated that production in the estuary corresponds to a fraction of .015 g/m^3/day of the ratio given by Sverdrup for plankton of O:C:N:P = 109:41:7.2:1. For nitrogen this is .015x7.2 or .108 g/m^3/day over a volume of 50×10^6 m^3 of water or 5.4×10^6 g/day.

14. It is assumed that about one half of the incoming radiation given in note 5 reaches the light storage compartment or 3.0×10^{10} kcal/day.

15. The light dispersed includes that which bounces off the plankton and that which never impinges on any plankton (a function of the concentration of chloroplasts). For the low standing crop here this is some large fraction of incoming light or 2.9×10^{10} kcal/day.

16. The light energy incorporated into phytoplankton biomass can be calculated from the bomb calorimeter value of organic matter, which is about 4.5 kcal/g. This multiplied by the productivity (42.7×10^6 g/day) is 1.92×10^8 kcal/day.

17. Production is given a starting value equal to standing crop (notes 4 and 11 of this table) or 42.7×10^6 g/day.

18. Phytoplankton exported includes that which goes downstream by advection and that which is deposited in the sediment. No recycle is included so that at steady state input = export or 42.7×10^6 g/day.

Notes to Table 6

1. Sources of numbers utilized frequently in calculating numerical values are:
   a) Area of Peninsular Florida = 10^{11} m^2; calculated by summing county areas given in Fla. Stat. Abst. (1971), and defined by the St. Mary's River on the northeast and the Suwannee River on the west.
   b) Population of peninsular Florida is 5,367,161 (Fla. Stat. Abst., 1971).
   c) Percent land in each of the four categories (given in Fla. Stat. Abst. by county, 1971)
      1' - naturally vegetated areas include sawgrass, commercial pine forests, tree farms, pasture land, and miscellaneous = 76.0%.
      2' - cropland includes fertilized farm land for citrus, field crops, and vegetables = 11.6%.
      3' - surface waters include lakes, rivers, and marshes with continuous standing water = 9.0%.
      4' - urban areas include only large cities -- Jacksonville, the "Gold Coast" through Miami, St. Petersburg, Tampa, and Orlando = 3.4%.
   d) Florida receives 150 BGD in rain (Pyne et al., 1967). Of this, 20% is dissipated as surface drainage and 10% as subsurface drainage (Sheffield, 1970) or 4.12×10^{13} 1/year as surface drainage and 2.06×10^{13} 1/year as subsurface drainage. From the percentage

of land in each of the four categories above (c), the runoff distribution for each is calculated:

	To Surface Water (l/year)	To Subsurface Water (l/year)
Natural Land	3.130×10^{13}	1.58×10^{13}
Cropland	$.478 \times 10^{13}$	$.262 \times 10^{13}$
Lakes and Marshes	$.371 \times 10^{13}$	$.208 \times 10^{13}$
Urban	$.140 \times 10^{13}$	0.0

2. The state of Florida used 45,975 million kilowatt hours in 1968 (Fla. Stat. Abst., 1971, p. 406). Peninsular Florida contains about 80% of the total population; assuming it uses 80% of the power, utilization is $36,780 \times 10^{6}$ kilowatt hours/year. Converting kilowatt hours to kilocalories yields $31,638 \times 10^{9}$ kilocalories/year ($36,780 \times 10^{6}$ x 860.2 kilocal/kilowatt hours). Dividing this by the area of peninsular Florida (10^{11} m^2) yields 316.4 kilocal/m^2/year.

5. 1,326,000 people have immigrated to Florida in the last ten years (Fla. Stat. Abst., 1972, p. 39) or 132,600 immigrants/year. The average person contains 100 g P (footnote 15) so that the influx of immigrants in terms of phosphorus is 13,260,000 g. Converting to mg and dividing by the area under consideration yields .1326 mg/m^2/year.

6. The daily requirement of phosphorus by people is 1.5 g/c/d (Stumm and Zollinger, 1972). For the 5,367,161 people living in the study area (Fla. Stat. Abst., 1972), this is a phosphorus demand of 8.05×10^6 g/day or 2.94×10^{12} mg/year. Florida crops supply 1.41×10^{12} mg/year (calculated in note 28); the remainder or 1.53×10^{12} mg/year must be imported. This is 15.3 mg/m^2 Fla./year.

7. The U.S. now consumes between 2.0 and 2.4 g P/c/d (Vollenweider, 1970). Using the conservative value of 2.0 g/c/d and multiplying it by the 5,367,161 people yields 10.73×10^6 g/day or 3.92×10^{12} mg/year. Dividing by the state area results in a requirement of 39.2 mg/m^2/year. Note 31 indicates that 81% of the people are served by sewage treatment plants and 19% by septic tanks, thus 31.75 mg/m^2/year goes to treatment plants and 7.45 mg/m^2/year to septic tanks.

8. Calculated in note 7 to be 7.45 mg/m^2/year. It is treated as a forcing function since additional population requires sewage treatment plant hookups.

9. The rainfall concentration for the Gainesville area is .033 mg P/l (Brezonik et al., 1969). An average rainfall of 50"/year (Bradley, 1972) over 10^{11} m^2 of land yields 1.27×10^{14} l/year of rain. Multiplying by the concentration yields 4.2×10^{12} mg/year. Dividing by the study area (10^{11} m^2) results in 42.0 mg/m^2/year.

Concentrations as high as .09 mg/l have been observed in the rain in the Lake Apopka area (Schneider and Little, 1969) so that 42.0 is a conservative estimate.

10. Where sea bird rookery and nesting coastal zones exist in the world, this could be a significant pathway. Presently in peninsular Florida none exist. Where birds such as cormorants do feed at sea and then come to land most of their defecation (Johnston, personal communication) occurs while they are flying at sea; they fertilize their own feeding ground.

11. The U.S. Army Corps of Engineers National Shoreline Study (1971) states that there is 593 miles of primary coast bordering the Atlantic Ocean with 1,723 miles of associated bay/estuary shoreline. The 673 miles of primary coast bordering the Gulf of Mexico has 3,276 miles of bay/estuary shoreline; 450 miles of this Gulf of Mexico primary coast is within the study area (Suwannee River to the south). The length of primary coast multiplied by an average width multiplied by a mean tidal range by the number of tides per day will yield the volume of water flowing in and out per day. An average width of 1/2 mile was chosen. An average tidal range for the Atlantic and Gulf coasts was determined by the tide tables (U.S. Dept. Commerce, 1972). The average mean tidal range for shoreline directly bordering open ocean on the Atlantic Coast is 3.2 feet

(twice a day). The mean tidal range (diurnal - once a day) for the shoreline bordering the open Gulf coast is 2.2 feet. Total volume input and output on the Atlantic coast is 5.3×10^{14} 1/year (593 miles x 5,280 feet/mile x 1/2 mile width x 3.2 feet tidal range x 2 tides/day x 365 days/year x 7.5 gallons/ft^3 x 3.78 1/gal). Total volume input and output on the Gulf coast is 1.4×10^{14} 1/year (450 miles x 5,280 feet/mile x 1/2 mile wide x 2.2 ft tidal range x 7.5 gal/ft^3 x 3.78 1/gal x 365 days/year). Total volume for both coasts is $5.3 \times 10^{14} + 1.4 \times 10^{14} = 6.7 \times 10^{14}$ 1/year. Graham (1954) and Alberts et al. (1970) give an ocean phosphorus concentration of .031 mg/1. Phosphorus input and output with the tide is 2.08×10^{13} mg/year (6.7×10^{14} 1/year x .031 mg/1). Dividing by the area under study (10^{11} m^2) yields 208 mg/m^2/year.

13. Elevation of the Eocene Ocala limestone in central Florida is 115 feet (Cooke, 1945). Assuming the Ocala limestone was deposited at sea level 50 million years ago yields an uplift rate of 2.3×10^{-6} ft/year. The problem here is to obtain the amount of phosphorus contributed to the stock of commercial grade rock (Pliocene - Bone Valley Foundation) as a result of uplift. Assume the Bone Valley formation with an areal extent of 6.54×10^{10} ft^2 (Cooke, 1945) is rising at this same rate due to isostatic adjustment; then, the

total rock addition in the pebble phosphate district is 15.0×10^4 ft^3/year (2.3×10^{-6} ft/year x 6.54×10^{10} ft^2) at a phosphorus content of 4.8% by volume or 7.2×10^3 ft^3 P/year or 3.7×10^8 g P/year (5.15×10^4 g/ft^3 x 7.2×10^3 ft^3/year) or 3.7×10^{11} mg P/year. Dividing by the area under study yields a final value of 3.7 mg/m^2/year.

14. Surface water entering the study area from Georgia enters by way of the Withlacoochee River at an average flow of 1,500 cfs or the Suwannee River at an average flow of 1,700 cfs. Adding and converting to the metric system yields a total inflow of 2.8×10^{12} l/year (3,200 cfs x 28.32 l/cf x 86,400 s/day x 365 days/year) at a concentration of .1 mg/l or $.28 \times 10^{12}$ mg/year or 2.8 mg/m^2/year.

15. Human cells are .134% P (Lehninger, 1970). This is 1.34 mg/g. At a 70 kg average weight per person or 70,000 grams, this is a phosphorus content of 93.8 g P/person. For a population of 5,367,161 people this is 5.03×10^8 grams or 5.03×10^{11} mg. Dividing by 10^{11} m^2 = 5.03 mg/m^2.

16. Assume that one-half day's sewage is stored in the treatment plants. At a phosphorus input of 3.5 g/c/d (human waste plus detergents, see footnotes 6 and 7), this is .094 mg/m^2 (3,500 mg/c/d x 1/2 day x 5,367,161 people divided by 10^{11} m^2).

17. The storage consists of the phosphorus in the soil and that in standing crop. The weight of Florida mineral soil six inches deep is $2x10^6$ lbs/acre (Blue, 1972, personal communication). The total phosphorus content of 435 soils averaged is .0834% (Gammon et al., 1953). The phosphorus content per acre, then, is 1,600 lbs P/acre ($2x10^6$x.0008). Converting to the metric system yields 179,500 mg/m^2. Assuming a 5-foot depth, this is a total phosphorus content of 1,795,000 mg/m^2. Assuming standing crop for sawgrass is 1,200 g/m^2 (Steward, 1971), for mangroves is 5,000 g/m^2 (Sell, personal communication), for pines is 3,000 g/m^2, and for pastureland is almost negligible, yields an average of 1,500 g/m^2 multiplied by a phosphorus content of .04% (Steward, 1971) or 600 mg/m^2. Total storage is 1,795,000 + 600 = 1,795,600 mg/m^2. Naturally vegetated area is 76% of the total area (footnote 1c) so that the final value is 1,364,656 mg/m^2 (1,795,600x7.6) or about 1,360,000 mg/m^2.

18. The storage consists of phosphorus in the soil and that in standing crop. There are 10,000 lbs/acre P_2O_5 in the cropland soils saturated with fertilizer (Westgate, Forbes, Blue, 1957) or .22% P in soils at $2x10^6$ lbs/acre. Phosphorus is 43.66% of P_2O_5 or 4,366 lbs P/acre on cropland. Converting to the metric system yields 489,786 mg/m^2. The citrus trees constitute the

only significant standing crop on cropland. Assuming a biomass of 2,000 g/m^2 x .04% P yields 800 mg/m^2. Total phosphorus is 489,786 + 800 = 490,586 mg/m^2. Cropland is 11.6% of the total land, yielding a final value of 55,748 mg/m^2.

19. In 1969 Florida mined 110,000,000 tons of phosphate rock (Bureau of Mines, 1969) of which the P_2O_5 content was 15,700,000 tons. Phosphorus is 43.7% of P_2O_5 or 6.86×10^6 tons of phosphorus mined; 6.86×10^6 tons of P is 6.2% of 110×10^6 tons of rock or 62 mg P/g rock. It is estimated that there is a 50-year supply of this grade rock (Env. Prot. Agency, 1971a). On that basis it is calculated that the storage of elemental phosphorus in commercial grade phosphate rock is 3.1×10^{14} g = 3.1×10^{17} mg (110×10^6 tons rock/year x 50 years x 2,000 lbs/ton x 454 g/lb x .062 g P/g rock). Dividing by the area under study (10^{11} m^2) yields a final value of 3.1×10^6 mg/m^2.

20. Florida Stat. Abst. (1971) gives the area under water for each county as 1×10^{11} ft^2. An average depth of 8 feet is calculated from data on North Central Florida Lakes (Brezonik et al., 1969) from the 13-foot depth of Lake Okeechobee plus rivers and many very shallow areas in the everglades. Volume is then 8×10^{11} ft^3 or 2×10^{13} l water. Averaging all of Odum's (1951) data for lakes, rivers, and marshes yields an average total P

concentration of .163 mg/1. Total phosphorus is $.326 \times 10^{13}$ mg (2×10^{13} x .163 mg/1) and dividing by the area under study (10^{11} m^2) yields 32.6 mg/m^2.

21. Most Florida type fertilizers are 31.5% phosphorus (Vollenweider, 1970). Footnote 19 shows a production of 6.86×10^6 tons of P per year. Sixty percent of production goes for agriculture (Sweeney and Maxwell, 1969), yielding a phosphorus content for fertilizers on a yearly basis of 4.1×10^6 tons P. It is assumed that there is one year's production in storage or 4.1×10^6 tons P. Converting to the metric system and dividing by the area under study yields a final value of 3.72×10^4 mg/m^2 (4.1×10^6 tons x 2,000 lbs/ton x 454 g/lb divided by 10^{11} m^2).

22. Assume an average thickness of 300 feet and a porosity of 20% for the Florida Aquifer (assorted Florida Geological Survey bulletins). Converting to the metric system and using .05 mg/l as the phosphorus concentration (Odum, 1951) yields a phosphorus storage of 9.1×10^{13} mg P (91.44 m thick x 10^{11} m^2 surface area x 20% porosity x 10^3 l/m^3 x .05 mg/l). Dividing by the area under study (10^{11} m^2) results in a final value of 910 mg/m^2.

23. The volume of water stored is estimated from data on width and depths of bays given by the U.S. Army Corps of Engineers (1971). There are 5,000 miles of estuarine

shoreline in Florida. This is divided in half to get an estimate of the sum of the lengths of all estuaries. There are 1,300 miles of primary coast; open water coasts are included as estuaries. The average width of all embayments is estimated to be one-half mile. Open water coasts are considered out to one-half mile (footnote 11). Average depth is 20 feet. Volume is length x width x depth or 3.0×10^{13} liters [(2,500 miles + 1,300 miles) x 5,280 ft/mile x $\frac{5,280}{2}$ wide x 20 ft deep x 7.5 gal/ft^3 x 3.78 l/gal]. The average phosphorus concentration of Florida's estuaries is .05 mg/l except for Charlotte Harbor and Hillsborough Bay where it is .35 mg/l. Charlotte Harbor and Hillsborough Bay contain 10^{11} liters of water or $.35 \times 10^{11}$ mg phosphorus. All others contain $.15 \times 10^{13}$ mg of phosphorus (3×10^{13} l x .05 mg/l). The total is $.1535 \times 10^{13}$ mg P ($.15 \times 10^{13}$ + $.0035 \times 10^{13}$). Dividing by the area under study (10^{11} m^2) yields a final value of 15.35 mg/m^2.

24. Average slime pond size is 1,000 acres at 20 feet deep (Specht, 1950). It is estimated that there are 50 such ponds for a total volume of 12.3×10^{11} liters slime water (50 ponds x 1,000 acres/pond x 43,560 ft^2/acre x 20 feet deep x 7.5 gal/ft^3 x 3.78 l/gal). The phosphorus concentration of slime water is 7,540 mg/l (Toler, 1967), resulting in a total phosphorus storage of 9.27×10^{15} mg. Dividing by the area under study (10^{11} m^2) yields a final value of 9.27×10^4 mg/m^2.

25. Most of the sludge from sewage treatment plants in Florida is dumped into sanitary landfills where it is reworked into the phosphorus cycle very slowly. On this time scale, then, no recycle pathway is shown. It is assumed here that a 10-year storage of unreworked sludge exists. At an influx rate of 16.66 mg/m^2/year (footnote 38) this is a storage of 166 mg/m^2.

26. The amount of total phosphorus in sediment is variable. It ranges from 200 to 2,000 mg/kg (.02 to .21%) for Lake Apopka (Schneider and Little, 1969) and from .05 to 1% for Anderson Cue Lake in North Central Florida (Brezonik et al., 1969). A conservative value of .05% is assumed here; the total storage is calculated for 5 feet of sediment (an average sediment thickness in Florida lakes), calculating on the basis of .05% P in 5 ft^3 of sediment (1' by 1' by 5') where sediment weighs about 2.2×10^5 g/m^2 for a 6" deep layer yields 9.8×10^{15} mg (2.2×10^5 g/m^2 - 6" deep x 10 for 5' x .0005 x .09 x 10^{11} m^2 of lake x 10^3 mg/g). Dividing by the area under study (10^{11} m^2) yields a final value of 98,000 mg/m^2.

26a. Assuming an average depth of 5 feet for the sediment and a sediment weight of 2.2×10^5 g/m^2 per acre half-foot depth or 4.4×10^5 g/m^2 per foot depth yields a sediment weight of 22.0×10^5 g/m^2 for the five feet. Phosphorus content of the sediment in Charlotte Harbor

and Hillsborough Bay averages 1.9% PO_4 by weight (Huang and Goodell, 1967, and FWPCA report, 1969). Other estuarine sediment averages .02% P by weight (Miller, 1952). Total estuarine area is 5.3×10^{10} ft^2 or 4.9×10^9 m^2 (note 23), of which .8% is in Charlotte Harbor and Hillsborough Bay. Taking a weighted average of the two populations yields a total phosphorus storage of 2.67×10^{12} g P (4.9×10^9 m^2 x 22.0×10^5 g/m^2 x .008 x .019 x 1/3) plus (4.9×10^9 m^2 x 22.0×10^5 g/m^2 x .992 x .0002). Converting to mg and dividing by the area under study (10^{11} m^2) yields a final value of 26,700 mg/m^2. Note that this is per m^2 of the study area; the actual storage is 2.67×10^{15} mg/4.9×10^9 m^2 or 545,000 mg/m^2.

27. People require 1.5 g P/cd (Stumm and Zollinger, 1972), resulting in an influx per year for people of 29.4 mg/m^2/year (1.5 g/cd x 5,367,161 people x 365 days/year x 10^3 mg/g divided by 10^{11} m^2 peninsular Florida).

28. Mr. J. Moore of the Florida Farm Bureau supplied data on the percent of production for field crops, citrus, and vegetables that is consumed within the state. The average percent from his data is 7.2% consumed. The crop production in Florida is 196.3 mg/m^2/year (detailed calculations in footnote 37). 7.2% of 195.2 mg/m^2/year is 14.1 mg/m^2/year.

29. Eighty-one percent of the people are on some kind of treatment plant hook-up (note 31). At a requirement

of 1.5 g P/cd the flux to treatment plants is 2.38×10^9 g = 2.38×10^{12} mg (1.5 g/cd x .81 x 5,367,161 people x 365 days/year x 10^3 mg/g). Dividing by the area under study (10^{11} m^2) results in a final value of 23.8 mg/m^2/year.

30. Nineteen percent of the people in peninsular Florida use septic tanks (note 31). At a requirement of 1.5 g P/cd the flux to septic tanks or to natural lands is 5.6×10^{11} mg (1.5 g/cd x .19 x 5,367,161 x 365 days/year x 10^3 mg/g). Dividing by the area under study (10^{11} m^2) results in a final value of 5.6 mg/m^2/year.

31. Eighty-one percent of the people in peninsular Florida are on some kind of treatment plant hook-up (Inventory of Sewerage Systems in Florida, 1966). This percent was calculated on the basis of a water usage of 100 gallons per person per day (McGauhey, 1968). The inventory gives the amount of water treated in millions of gallons per day and the locality of effluent discharge. Total effluent going into estuaries in peninsular Florida is 345 MGD and to inland waterways is 86 MGD. Converting to numbers of people yields 4,310,000 people (345×10^6 gal/day divided by 100 gal/person/day) or 81% of the total population (5,376,161 people). The water usage now is thought to be 120 gal/person/day (Furman, personal communication);

however, the lower value of 100 gal/cd was used in the calculation to compensate for the 1966 treatment plant data. The number of people whose effluent enters estuaries is 65% of the total population (3.45×10^6 divided by 5,367,161). Using the standard phosphorus concentration of 5.2 mg/l in secondarily treated sewage and converting to the metric system yields a phosphorus influx to estuaries of 3.0×10^{12} mg/year (5.2 mg/l x 120 gal/person/day x 3.78 l/gal x .65 of 5,367,161 people/day x 365 days/year). Dividing by the area under study (10^{11} m^2) yields a final value of 30.0 mg/m^2/year.

32. Note 31 shows that the treated sewage effluent from $.86 \times 10^6$ people or 16% of the total population enters surface waters. At 5.2 mg P/l, this corresponds to 7.4×10^{11} mg/year (5.2 mg/l x 120 gal/person/day x 3.78 l/gal x $.86 \times 10^6$ people x 365 days/year). Dividing by the area under study (10^{11} m^2) yields a final value of 7.4 mg/m^2/year.

34. Stumm and Zollinger (1972) give an average value of .01 g/m^2/year for runoff from forests, meadows, and grasslands. This converts to 10 mg/m^2/year multiplied by the percent of natural lands (76%) or 7.6 mg/m^2/year. Brezonik et al. (1969) give values of .018 g/m^2/year for pastureland and .008 g/m^2/year for forested areas in Florida. Since there are about equal areas of each,

the average value of .013 g/m^2/year = 13 mg/m^2/year results in a final value of 9.88 mg/m^2/year (13 mg/m^2/year x 76%). A higher average value for Florida than for the world should be expected.

35. Fertilizer use in Florida is 98,707 tons P_2O_5 per year (NeSmith, 1968-71) multiplied by 43.6% for elemental phosphorus yields 43,036.2 tons. About 5% of this is used in the state outside the study area (west of the Suwannee River), leaving 40,884.4 tons (43,036.2 - 2,151.8) used in peninsular Florida. Converting to the metric system yields 3.7×10^{13} mg P applied to croplands yearly (40,884.4 tons x 2,000 lbs/ton x 454×10^3 mg/lb). Dividing by the area under study (10^{11} m^2) results in a final value of 370 mg/m^2/year. This value compares well with that given by Heaney et al. (1971) of 27.8 lb P/acre = 362 mg/m^2/year (27.8 lb/acre x 454 x 10^3 mg/lb divided by 4,047 m^2/acre x .116% of land area).

36. Values for this pathway range from .018 - .135 g/m^2/year (Brezonik et al., 1969) to .56 - 2.3 g/m^2/year (Biggar and Cory, 1969) to 1.12 g/m^2/year (Dept. of Agriculture, 1970) to 18.4 g/m^2/year (Heaney et al., 1971). From reading many papers including the above on the subject, an educated guess is made. On the basis of .5 g/m^2/year = 500 mg/m^2/year is calculated the final value of 58 mg/m^2/year (500 x 11.6% of total land is cropland).

For comparison, many sources give 1 mg/l as the phosphorus concentration of agricultural runoff. The surface runoff from agricultural land in Florida (note 1d) is 47.8×10^{11} l/year or 47.8×10^{11} mg divided by 10^{11} m^2 in study area = 47.8 mg/m^2/year, a value which agrees quite well with the 58 mg/m^2/year calculated above for Florida.

37. Total phosphorus removed in crops is 15 lb/acre/year. This figure was obtained by multiplying yields per acre (Florida Almanac, 1972) by the phosphorus content corresponding to that yield (Donahue et al., 1971, for field crops and Howard et al., 1962, for vegetables). Fifteen pounds per acre is 1,683 mg/m^2 (15 lb/acre x 454 x 10^3 mg/lb divided by 4,047 m^2/acre); 1,683 mg/m^2 x 11.6% of total land as cropland is 195.2 mg/m^2/year. Of this, 14.1 mg/m^2/year is consumed in Florida (note 28) so that 181.1 mg/m^2/year is exported.

38. The P_2O_5 content of Florida rock used or sold by producers annually is 9,603,000 tons (U.S. Bureau of Mines, 1969). This converts to 4,187,000 tons of elemental phosphorus used or sold ($.436 \times 9.6 \times 10^6$). Sixty percent of production is for agriculture (U.S. Bureau of Mines, 1969) or 2,510,000 tons P. Converting to metric units yields 2.28×10^{15} mg (2.5×10^6 tons x 454×10^3 mg/lb x 2,000 lb/ton). Dividing by the area under study (10^{11} m^2) results in a final value of 2.28×10^4 mg/m^2/year. Since 370 mg/m^2/year is applied to Florida

cropland (note 35), the algebraic difference or 2.24×10^4 mg/m^2/year is exported from the study area.

39. The number is calculated by multiplying the surface runoff by the concentration. Surface runoff is 4.12×10^{13} l/year (note 1d). The average of all of Odum's (1951) values for rivers except the Peace and Alafai is .18 mg/l. Concentrations in the Peace and Alafai Rivers averages 2.33 mg/l. A weighted average of the two multiplied by their respective volumes yields an annual runoff of phosphorus of 1.12×10^{13} mg/year ($.138 \times 10^{13}$ l/year x 2.33 mg/l for Peace and Alafai Rivers plus 4×10^{13} l/year x .18 mg/l for the remainder). Dividing by the area under study (10^{11} m^2) yields a final value of 102 mg/m^2/year.

40. The American Chemical Society (1969) states that there is 30% phosphorus removal in secondary treatment. Thirty percent of the incoming rate of 55.55 mg/m^2/year yields 16.66 mg/m^2/year.

41. Water exported is the sum of the tide out plus the net river discharge. Tidal output is 6.7×10^{14} l/year (note 11) and river discharge is 4.12×10^{13} l/year (note 1d). Phosphorus concentration of the estuaries is .05 mg/l except in Charlotte Harbor where it is .35 mg/l. A weighted average of each yields a total discharge to the ocean of $.37 \times 10^{14}$ mg/year ($.05 \times 10^{14}$ l/year x .35 mg/l plus 7.112×10^{14} l/year x .05 mg/l).

Dividing by the area under study (10^{11} m^2) results in a final value of 370 mg/m^2/year.

42. Mining effluent to the Peace River is $1.3x10^9$ 1/day at 1 mg/1 and from the Alafai is $.5x10^9$ 1/day at 2.5 mg/1 or a total phosphorus discharge of $2.55x10^9$ mg/day = $9.3x10^{11}$ mg/year. Dividing by the area under study (10^{11} m^2) yields a final value of 9.3 mg/m^2/year. For comparison and perspective the discharge from the 1971 slime spill into the Peace River was $2.2x10^{14}$ mg phosphorus or in the units of the model 2,200 mg/m^2.

43. The U.S. Bureau of Mines (1969) indicates that 60% of the phosphorus mined goes to agriculture, 38% is exported from the state mostly for phosphoruc acid and 2% goes to other industrial users. This pathway, then, is 40% of the 4,187,000 tons of elemental phosphorus mined (note 38) or $1.67x10^6$ tons exported. Converting to the metric system yields $1.516x10^{15}$ mg P ($1.67x10^6$ tons x 2,000 lb/ton x $454x10^3$ mg/lb). Dividing by the area under study (10^{11} m^2) results in a final value of $1.52x10^4$ mg/m^2/year.

44. Slime constitutes one-third of the total matrix mined (Env. Prot. Agency, 1971b) or 1/3 of 110,000,000 tons per year ($36.3x10^6$ tons) with an average P_2O_5 content on dry basis of 11.8% or an average elemental P content of 5.15%. Multiplying and converting to the metric system yields $1.7x10^{15}$ mg P ($36.3x10^6$ tons x .0515

x 2,000 lbs/ton x 454×10^3 mg/lb). Dividing by the area under study (10^{11} m^2) results in a final value of 17,000 mg/m^2/year. Other losses in washer and flotation operations amount to 8,000 mg/m^2/year (EPA report, 1971).

45. The contribution of phosphorus from urban runoff has been estimated as .110 g/m^2/year (Brezonik et al., 1969, from Weibel, 1969) or 110 mg/m^2/year. Urban land as calculated in footnote 1 constitutes 3.4% of the land under study so that the final value is 3.74 mg/m^2/year (110 x .034).

46. There is general agreement (Stumm and Leckie, 1971) that, although the phosphorus in sediment and in overlying waters is in a dynamic exchange condition, on a balance a fraction of phosphorus becomes irretrievably lost in the sediment. For Stumm's hypothetical lake (Stumm and Zollinger, 1972), the annual loss to sediment is .18 mg P/l. For lakes averaging 50 m deep, discussed by Vollenweider (1970), the loss is 1.4 mg P/m^2/day. Converting to the proper units results in 36 mg/m^2/year for Stumm's lake and 46 mg/m^2/year for Vollenweider's lake (for Stumm's lake: .18 mg/l x 2 x 10^{13} l surface water in Florida divided by 10^{11} m^2 in study area; for Vollenweider's lake: 1.4 mg/m^2/day x 365 days/year x 9% of total land in surface water). The conservative value of 36 mg/m^2/year is chosen,

although the rate may be higher in Florida due to accelerated eutrophication rates.

47. Water flux in and out of groundwater for each land type multiplied by the phosphorus concentration yields the phosphorus flux for each category. The concentration of water that becomes part of the aquifer is assumed to be .05 mg/1 (Odum, 1951), although the concentration of water leaving each land type is higher than .05 mg/1. The excess phosphorus is deposited in the subsoil before the water reaches the aquifer. This implies that a buildup of phosphorus in natural lands and croplands is expected. All water fluxes are from footnote 1.

Natural land to groundwater: 1.58×10^{13} 1/year $\times$ .05 mg/1 $\div 10^{11}$ m^2 = 7.9 mg/m^2/year.

Cropland to groundwater: $.262 \times 10^{13}$ 1/year $\times$ .05 mg/1 $\div 10^{11}$ m^2 = 1.3 mg/m^2/year.

Surface water to groundwater: $.208 \times 10^{13}$ 1/year $\times$ .05 mg/1 $\div 10^{11}$ m^2 = 1.0 mg/m^2/year.

Groundwater to surface water: $.25 \times 10^{13}$ 1/year $\times$ .05 mg/1 $\div 10^{11}$ m^2 = 1.0 mg/m^2/year.

Groundwater to ocean: 2.06×10^{13} 1/year $\times$ .05 mg/1 $\div 10^{11}$ m^2 = 10.3 mg/m^2/year.

48. Measurements of phosphorus in the air are scarce and measurements of phosphorus in smoke are scarcer. The underbrush of tree farms in Florida is burned about every 5 years. Assuming an underbrush biomass of

500 g/m^2 at .04% P yields an input to the air from burning of 11.0×10^{11} mg P (6,830,150 acres in tree farms from Fla. Stat. Abst., 1971, x 1/5 x 4,047 m^2/acre x 500 g/m^2 x .0004 P x 10^3 mg/g). The only other burning of any consequence occurring in the state is in the Everglades, which burns about once every 8 years (Bayley, personal communication). Assuming a sawgrass biomass of 1,000 g/m^2 at .036% P (Steward, 1971) yields a phosphorus input of 2.5×10^{11} mg P (1,400,533 acres x 1/8 x 1,000 g/m^2 x 4,047 m^2/acre x .00036 x 10^3 mg/g). Total input from tree farms burning and burning in the Everglades is 13.5×10^{11} mg P. Dividing by the area under study (10^{11} m^2) yields a final value of 13.5 mg/m^2/year.

49. The phosphorus concentration of rain in the Zellwood farming district, which is highly fertilized, is .08 mg/l (Schneider and Little, 1969); the average for other areas is .03 mg/l. From this difference a rough estimate of the phosphorus input to the air through dust from highly fertilized cropland can be made. The difference of .05 mg/l yields an input of 63.5 mg/m^2/year on the cropland (50 inches of rain x .024 m/in = 1.27 m/m^2 or 1.27 m^3/m^2 or 1,270 l/m^2 x .05 mg/l). Only .05% of the total Florida land is heavily fertilized (Fla. Atlas, 1964), yielding a final value in the units of the model of 3.2 mg/m^2/year.

50. The annual fish catch from estuaries is 147,115,000 lbs (Fla. Stat. Abst., 1971, p. 368) at a phosphorus concentration of .1% which yields 6.68×10^{10} mg P/year (147,115,000 lbs x .001 x 454 x 10^3 mg/lb) or .668 mg/m^2/year when distributed over the study area of 10^{11} m^2.

51. Rates of net deposition are little known and at best highly variable. Pomeroy (1972) gives values from 1 to 2 mg/m^2/day. Taking an intermediate value of 1.5 mg/m^2/day yields a total of 2.682×10^{12} mg/year [1.5 mg/m^2/day x 365 days/year x 4.9 x 10^9 m^2 (footnote 26a)]. Dividing by the area under study (10^{11} m^2) yields a final result of 26.8 or 27 mg/m^2/year.

Notes to Table 8

1. The density of limestone is 1.3×10^6 g/m^3. Assuming it is initially 90% $CaCO_3$ (Cooke, 1945), this is 1.17×10^6 g/m^3 $CaCO_3$ or ÷ 100 g/mole = 1.17×10^4 moles/m^3 or 1.17×10^7 mmoles/m^3. The system includes 100 feet of rock or 30.48 meters so that the total storage is 35.6×10^7 mmoles/m^2 (1.17×10^7 mmoles/m^3 x 30.48 m).
2. Assuming the limestone is initially 1% $CaPO_4$ (Cooke, 1945), this is equivalent to 1.3×10^4 g/m^3 (1.3×10^6 g/m^3 limestone x .01). Converting to mmoles/m^3 and multiplying by the depth of storage yields 2.9×10^6 mmoles/m^2 (1.3×10^7 mg/m^3 ÷ 135 mg/mmole x 30.48 m).
3. The amount of HCO_3^- in percolating water can be calculated by multiplying the quantity of water which percolates through in one year by the concentration. Groundwater percolation in Florida averages 200 l/m^2 (Pyne et al., 1967) and the HCO_3^- concentration is 200 mg/l (U.S. Geol. Surv., 1961-1968), yielding a storage in one year of 40,000 mg/m^2 ÷ 61 mg/mmole = 655.73 mmoles/m^2.
4. The amount of $HPO_4^=$ in percolating water is 200 l water/m^2 percolating through multiplied by .3 mg $HPO_4^=$/l (Odum, 1951) or 60 mg/m^2 ÷ 96 mg $HPO_4^=$/mmole = .625 mmole/m^2.
5. Average rainfall in Florida is 50 inches/year or 1,270 l/year (Bradley, 1972) and the phosphorus concentration

of rain is .04 mg P/l; it varies from .03 to .09 mg/l (Brezonik et al., 1969, and Schneider and Little, 1969). Volume of water per year multiplied by phosphorus concentration yields 1.64 mmoles/m^2/year (1,270 l/year x .04 mg/l ÷ 31 mg P/mmole).

6. The isostatic adjustment rate is made equal to .03 m/1,000 years, a value which is required to maintain a constant elevation for Florida under the conditions of this model; that is, the number was back calculated using the analog computer when the model was run. The number is the same order of magnitude as estimates by Rusnak (1967) and calculations done previously on page 188 of this report. The $CaCO_3$ contribution is 350 mmoles/m^2/year ($1.3x10^9$ mg limestone/m^3 x .9 ÷ 100 mg/mmole x $.03x10^{-3}$ m uplift/year).
7. Using the same uplift rate estimated in footnote 6 and assuming that for initial conditions $CaPO_4$ is .5% of the rock mass being uplift yields a rate of 1.5 mmoles/m^2/year ($1.3x10^9$ mg limestone/m^3 x .005 ÷ 135 mg/mmole x $.03x10^{-3}$ m uplift/year).
8. Surface water runoff for Ca^{++}, HCO_3^-, $HPO_4^=$: Surface runoff in Florida averages 400 l/m^2/year (Pyne et al., 1967). Average Ca^{++} concentration of runoff is 10 mg/l (U.S. Geol. Surv., 1961-1968), HCO_3^- concentration is 80 mg/l (U.S. Geol. Surv., 1961-1968), and $HPO_4^=$ concentration is .3 mg/l (Odum, 1951). Multiplying the water runoff by the concentration and converting

to mmoles gives the final values:

Ca^{++} 10 mg/1 x 400 $1/m^2$/year ÷ 40 mg/mmole

= 100 mmoles/m^2/year

HCO_3^- 80 mg/1 x 400 $1/m^2$/year ÷ 61 mg/mmole

= 525 mmoles/m^2/year

$HPO_4^=$ .31 mg/1 x 400 $1/m^2$/year ÷ 96 mg/mmole

= 1.3 mmoles/m^2/year

9. Groundwater exports for Ca^{++}, HCO_3^-, $HPO_4^=$: Groundwater runoff for Florida averages 200 $1/m^2$/year (Pyne et al., 1967). Average Ca^{++} concentration for runoff is 70 mg/1 (Odum, 1957), HCO_3^- concentration is 200 mg/1 (Odum, 1957), and $HPO_4^=$ concentration is .155 mg/1 or .05 mg/1 P (Odum, 1957). Multiplying the runoff by the concentration and converting to mmoles gives the final values:

Ca^{++} 70 mg/1 x 200 $1/m^2$/year ÷ 40 mg/mmole

= 350 mmoles/m^2/year

HCO_3^- 200 mg/1 x 200 $1/m^2$/year ÷ 61 mg/mmole

= 655.7 mmoles/m^2/year

$HPO_4^=$ .155 mg/1 x 200 $1/m^2$/year ÷ 96 mg/mmole

= .32 mmoles/m^2/year

10. Assuming a steady state, the amount of $HPO_4^=$ that comes from dissolving $CaPO_4^-$ can be calculated.

(in mmoles/m^2/year)

		OUT	IN	
$HPO_4^=$	surface runoff (footnote 8)	1.3	1.64	rain (footnote 5)
$HPO_4^=$	groundwater (footnote 9)	.32	y	dissolving $CaPO_4$
$HPO_4^=$	reprecipitation	.32		
		1.94 =	1.64 + y	

y = .30

11. Rates for the amount of HCO_3^- introduced to the system through respiration in the soil, the quantity of HCO_3^- contributed from dissolving $CaCO_3$, and the quantity of HCO_3^- fixed as $CaCO_3$ in reprecipitation are calculated by assuming a steady state and solving two equations (for Ca^{++} budget and HCO_3^- budget) with two unknowns simultaneously. Note that the HCO_3^- introduced to the system from respiration is equal to that contributed by dissolving $CaCO_3$. The reason is made clear by the stoichemistry of the process.

$$H_2O + CO_2 \rightleftarrows H^+ + HCO_3^-$$

$$+ \qquad \text{and finally } 2HCO_3 + Ca^{++}$$

$$CaCO_3 \rightleftarrows Ca^{++} + HCO_3^-$$

For each HCO_3^- introduced from respiration one H^+ is available to dissolve one $CaCO_3$ producing one more HCO_3^-. The equations to be solved become:

(in mmoles/m^2/year)

		OUT	IN	
HCO_3^-	surface runoff (footnote 8)	524	x_2	dissolved from $CaCO_3$
HCO_3^-	groundwater runoff (footnote 9)	655.7	x_2	from respiration
HCO_3^-	reprecipitated	x_1		
		1,179.7 + x_1	= $2x_2$	

and		OUT	IN	
Ca^{++}	surface runoff (footnote 8)	100	47.6	rain*
Ca^{++}	groundwater (footnote 9)	350	x_2	dissolved from $CaCO_3$
Ca^{++}	reprecipitated as $CaCO_3$	x_1	.3	dissolved from $CaPO_4$
Ca^{++}	reprecipitated as $CaPO_4$ (footnote 10)	.32		
		450.32+x_1	= 47.9+x_2	

Two equations $1,179.7 + x_1 = 2x_2$

$450.32 + x_1 = 47.9 + x_2$

Solving simultaneously:

$x_1 = 374.86$ (reprecipitated HCO_3^-)

$x_2 = 777.3$ (dissolved from $CaCO_3$ and introduced from respiration)

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*Ca^{++} rain at 1.5 mg/l and 1,270 l/m^2/year (50" from Bradley, 1972) = 1,905 mg/m^2/year ÷ 40 mg/mmole = 47.6 mmoles/m^2/year.

Notes to Tables 9 and 10

a. Florida Statistical Abstract (1971).

b. Gross primary production estimated from measurements of similar areas from published literature.

c. Either calculated for Polk County or as the product of acres and gross primary production per acre.

d. Annual contribution in dollar equivalents estimated by dividing work for the county (note c) by 10,000 kilocal/$, which is the ratio of GNP to fuel usage in the U.S. economy (H. T. Odum, personal communication).

e. At the present production rate of 110×10^6 tons rock/year, 4,500 acres are stripped per year (Mr. Homer Hooks of the Florida Phosphate Council, personal communication) or 24,660 tons rock/acre. Total rock mined is $1{,}694 \times 10^6$ tons (U.S. Bur. Mines, 1930-1970) or 68,000 acres with 3/4 in Polk County or 50,000 acres.

f. E. P. Odum, 1971, p. 51.

g. Pinelands metabolism from Woodwell (1968) is 40 kilocal/m^2/day or 60×10^6 kilocal/acre/year.

h. Pasture metabolism is 2,500 kilocal/m^2/year (E. P. Odum, 1971) or 10.1×10^6 kilocal/acre/year.

i. From Odum, Littlejohn, and Huber (1972).

j. Taken as half of pasture metabolism (note e).

k. Supplied by Florida Power to Polk County, excluding mining industry, is 493×10^6 KWH or (at 860.5 kilocal/KWH) 4.2×10^{11} kilocal/year (Peyton of Florida Power, personal communication).

Supplied by Tampa Electric to Polk County, excluding mining industry, is 6.6×10^{11} kilocal/year (Mr. Bill Campbell of Rates and Research, Tampa Electric, personal communication).

Lakeland and Bartow with a population of 110,000 supply their own. At 10,000 KWH/person (Fla. Stat. Abst., 1971) this is 9.46×10^{11} kilocal/year.

Total electricity to Polk County, excluding that used by the mining industry, is $4.2+6.6+9.46 \times 10^{11}$ or 20×10^{11} kilocal/year.

l. Personal communication by letter from Mr. C. F. Guinn of Florida Gas gives 9.5×10^{12} BTU per year for 1972 or 23.9×10^{11} kilocal/year.

m. Kerosene used in Polk County in 1972 is 4,398,527 gallons (Mr. Ray Rutledge, Revenue Officer, Tallahassee, personal communication). At 3.86×10^{3} mg/gal, .7 g/ml, and 10 kcal/g, this is 1.2×10^{11} kilocal/year.

n. The LP and propane gas supplied statewide in 1972 was 350×10^{6} gal (Sid Stapleton, personal communication). Polk County represents 1/35 of the state's population or a use of 10×10^{6} gal. At .7 g/ml and 10 kcal/g, this is 2.7×10^{11} kcal/year.

o. 126,056,460.9 gal/year used in Polk County (Mr. Lew Thomas, State Department, Tallahassee, personal communication). At 3.86×10^{3} ml/gal, .7 g/ml, and 10 kcal/g, this is 34.0×10^{11} kilocal/year.

p. 2,500 kcal/person/day x 365 days/year x 227,222 people = 2.0×10^{11} kilocal/year.

q. Personal communication by letter from Mr. C. F. Guinn of Florida Gas gives 7.5×10^{12} BTU for 1972 or 18.9×10^{11} kilocal/year.

r. Tampa Electric (Mr. Bill Campbell, personal communication) supplies 1,634,393,000 KWH/year to phosphate industry; Florida Power (Mr. Peyton) supplies 839,000,000 KWH/year to phosphate industry. Summing and multiplying by 860.5 kcal/KWH yields 21.0×10^{11} kilocal/year.

APPENDIX B

MODELING DATA AND COMPUTER PROGRAMS

Some General Characteristics of Modeling with the Energy Circuit Language*

1. The three laws of thermodynamics hold for all processes.
2. Two levels of force may be represented--the single force and the population force. The single force is made up of component forces which are additive (electrical cells in series). The population force results from parallel actions of small forces where the flux is proportional to the number of forces.
3. A storage delivers a force to a pathway in proportion to the quantity stored; that is, there is linearity in each single pathway.
4. The outflow of intersections between pathways of energy flow requires energy from both inflows so that the outflow cannot occur without both inflows. For a multiplicative intersection, one energy flow controls the other in compliance with its driving force which is linear. Although the resulting pathways may be complex nonlinear processes, they may be broken down into linear component pathways.

Other assumptions for these models:

1. The transfer coefficients (k) or the fraction of storages which are transferred out by an outflow pathway are assumed constant throughout the time period of the model.

---

*See Odum (1972) for a detailed description.

2. Each system variable is considered constant al
the system at any given instant of time; there
"lumping" of matter and energy is allowed, res
a set of ordinary differential equations.

Peace River - Charlotte Harbor Estuarine System (Figs. 9 and 10)

```
PARAM R1=7.56E6,RA=1.0E4,R2=8.0,A4=1.78E7,A6=1.468E8,
                A8=1.871E8,Z=1.9
PARAM J1=52.36,J2=5.0,J3A=9.03E2,J3B=4.86,J3C=7540.0,
                J3D=1.0,J4=7.0
PARAM J6=1.5,J7=347.2,J8=.35,J9=1.52E-1,J10=3.8E7,
                J11=1.8E-2,J12=6.6E8
PARAM J13=1.8E-2,J14=1.15E9,J16=.031,C5=4.809E3,C6=1.29,
                C7=3.79E-5
PARAM C8=1.56E-7,C9=4.809E3,C11=3.37E3,C12=3.37E3,C13=5.68E-4
PARAM C14=5.65E-9,C16=9.51E3,C18=9.51E3,C19=7.98E-4,
                C20=3.0E-9,D=2.87
PARAM RAIN=3504.7
INCON Q4Z=2.66E7,Q5Z=1.597E7
INCON Q6Z=4.67E8,Q7Z=1.63E+8,Q8Z=5.38E8,Q9Z=1.34E+8
INCON Q10Z=1.57E10,Q11Z=4.3E11,Q12Z=5.5E11
      H=.396*SINE(0.0,4.363E-3,4.71239)
      J5=3435.*SINE(0.0,1.234E-5,4.71239)
      X1=Q6/A6
      X2=Q4/A4+Z
      Q4=INTGR(Q4Z,J1+J3A+(RAIN+J5)-C5*(X2-X1))
      Y3=COMPR(X1,X2)
      Y4=1-Y3
      X3=Q5/Q4
      Y5=COMPR(X3,R2)
      Q5=INTGR(Q5Z,J1*J2+J3D*J3A+J6*(RAIN+J5)...
      -C10*Q7/Q6*(X2-X1)*Y3-C6*Q5*Y5...
      -C7*J9*Q5+C8*J10*Q10-C9*X3*(X2-X1)*Y4)
      X4=Q8/A8
      Y6=COMPR(X4,X1)
      Y7=1-Y6
      Q6=INTGR(Q6Z,J7+C5*(X2-X1)-C11*(X1-X4))
      Q7=INTGR(Q7Z,J7*J8+C9*Q5/Q4(X2-X1)*Y4+C10*Q7/Q6*
               (X2-X1)*Y3*Y6...
      -C12*Q7/Q6*(X1-X4)*Y4*Y7-C15*Q9/Q8*(X1-X4)*Y6...
      -C13*J11*Q7+C14*J12*Q11)
      X5=H+D
      Q8=INTGR(Q8Z,C11*(X1-X4)-C16*(X4-X5))
      Y8=COMPR(X5,X4)
      Y9=1-Y8
      Q9=INTGR(Q9Z,C12*Q7/Q6*(X1-X4)*Y7+C15*Q9/Q8*
               (X1-X4)*Y8*Y6...
      -C17*J16*(X4-X5)*Y8-C18*Q9/Q8*(X4-X5)*Y9*Y7...
      -C19*J13*Q9+C20*J14*Q12)
      Q10=INTGR(Q10Z,C7*J9*Q5-C8*J10*Q10+C6*Q5*Y5)
      Q11=INTGR(Q11Z,C13*J11*Q7-C14*J12*Q11)
      Q12=INTGR(Q12Z,C19*Q9*J13-C20*J14*Q12)
```

Peace River - Charlotte Harbor Estuarine System
(No Daily Tide)

```
PARAM R1=7.56E6,R2=8.0,A4=1.78E7,A6=1.468E8,A8=1.87E8,Z=1.9
PARAM J1=75.4E3,J2=5.0,J3A=1.3E6,J3B=7000.,J4=7.0,J7=5.0E5
PARAM J8=.35,J16=.031,J9=1.52E-1,RAIN=5.0E6,H=-.10
PARAM C5=6.92E6,C6=1.88E3,C9=6.92E6,C11=4.85E6
PARAM C12=4.85E6,C16=1.36E7,C18=1.36E7
PARAM D=2.87,J6=1.5,RA=1.0E4,J3C=7.54E3,J3D=1.0
PARAM C7=.0548,C8=1.5E-7,J10=56.0,C13=.819,J11=1.8E-2,
              C14=5.8E-9
PARAM J12=957.,C19=1.15,C20=3.0E-9,J13=1.8E-2,J14=1665.
INCON Q4Z=2.66E7,Q5Z=1.597E7
INCON Q6Z=4.67E8,Q7Z=1.63E+8,Q8Z=5.38E8,Q9Z=1.34E+8
INCON Q10Z=1.57E10,Q11Z=4.3E11,Q12Z=5.5E11
      R5=4.9E6*SINE(0.0,.017453,4.71239)
      X1=Q6/A6
      X2=Q4/A4+Z
      Q4=INTGR(Q4Z,J1+J3A+(RAIN+R5)-C5*(X2-X1))
      X3=Q5/Q4
      Q5=INTGR(Q5Z,J1*J2+J3D*J3A+J6*(RAIN+R5)...
      -C6*Q5*Y5...
      -C7*J9*Q5+C8*J10*Q10-C9*X3*(X2-X1))
      X4=Q8/A8
      Q6=INTGR(Q6Z,J7+C5*(X2-X1)-C11*(X1-X4))
      Q7=INTGR(Q7Z,J7*J8+C9*Q5/Q4*(X2-X1)...
      -C12*Q7/Q6*(X1-X4)...
      -C13*J11*Q7+C14*J12*Q11)
      X5=H+D
      Q8=INTGR(Q8Z,C11*(X1-X4)-C16*(X4-X5))
      Q9=INTGR(Q9Z,C12*Q7/Q6*(X1-X4)...
      -C18*Q9/Q8*(X4-X5)...
      -C19*J13*Q9+C20*J14*Q12)
      Q10=INTGR(Q10Z,C7*J9*Q5-C8*J10*Q10+C6*Q5*Y5)
      Q11=INTGR(Q11Z,C13*J11*Q7-C14*J12*Q11)
      Q12=INTGR(Q12Z,C19*Q9*J13-C20*J14*Q12)
      A=Q7/Q6
      B=Q9/Q8
```

K Values Calculated for Fig. 9
for Use with Program No. 1

K	Value	K	Value
K_3	.529	K_{13}	.819
K_5	4.69×10^{7}	K_{14}	5.8×10^{-9}
K_6	1.88×10^{3}	K_{15}	1.7×10^{9}
K_7	.0548	K_{16}	1.03×10^{9}
K_8	1.5×10^{-7}	K_{17}	1.03×10^{9}
K_9	4.69×10^{7}	K_{18}	7.5×10^{8}
K_{10}	1.13×10^{8}	K_{19}	1.15
K_{11}	5.46×10^{8}	K_{20}	3.0×10^{-9}
K_{12}	5.46×10^{8}		

K Values Calculated for Fig. 9
for Use with Program No. 2

K	Value	K	Value
K_3	.529	K_{12}	4.853×10^{6}
K_5	6.926×10^{6}	K_{13}	.819
K_6	1.88×10^{3}	K_{14}	5.8×10^{-9}
K_7	.0548	K_{16}	1.369×10^{7}
K_8	1.5×10^{-7}	K_{18}	1.369×10^{7}
K_9	6.926×10^{6}	K_{19}	1.15
K_{11}	4.853×10^{6}	K_{20}	3.0×10^{-9}

Example Results of Simulation of Fig. 9
with Computer Program No. 2

IBM 1800 Computer - Digital Simulation Language

Time step - 1 day

Time run - 5 years

Print interval - 30 days

Parameter	Iteration 90	180	1080	1710
Q_4	$.5009 \times 10^8$	$.9106 \times 10^8$	$.4075 \times 10^8$	$.7973 \times 10^8$
Q_5	$.6823 \times 10^8$	$.1261 \times 10^9$	$.4592 \times 10^8$	$.1065 \times 10^9$
Q_6	$.5672 \times 10^9$	$.7959 \times 10^9$	$.5787 \times 10^9$	$.7918 \times 10^9$
Q_7	$.3300 \times 10^9$	$.6033 \times 10^9$	$.2926 \times 10^9$	$.5433 \times 10^9$
Q_8	$.5648 \times 10^9$	$.6410 \times 10^9$	$.5826 \times 10^9$	$.6522 \times 10^9$
Q_9	$.1630 \times 10^9$	$.2633 \times 10^9$	$.1929 \times 10^9$	$.2742 \times 10^9$
Q_{10}	$.1571 \times 10^{11}$	$.1578 \times 10^{11}$	$.1633 \times 10^{11}$	$.1671 \times 10^{11}$
Q_{11}	$.4300 \times 10^{12}$	$.4304 \times 10^{12}$	$.4343 \times 10^{12}$	$.4370 \times 10^{12}$
Q_{12}	$.5500 \times 10^{12}$	$.5501 \times 10^{12}$	$.5519 \times 10^{12}$	$.5531 \times 10^{12}$

Peace River - Charlotte Harbor Estuarine System
(Slime Spill)

```
PARAM R1=7.56E6,R2=8.0,A4=1.78E7,A6=1.468E8,A8=1.87E8,Z=1.9
PARAM J1=52.36,J2=5.0,J3A=9.03E2,J3B=4.86,J3C=7540.0,
              J3D=1.0,J4=7.0
PARAM J6=1.5,J7=347.2,J8=.35,J9=1.52E-1,J10=.0380,
              J11=1.8E-2,J12=.66
PARAM J13=1.8E-2,J14=1.1500,J16=.031,C5=4.809E3,C6=.200,
              C7=3.79E-5
PARAM C8=1.56E-7,C9=4.809E3,C11=3.37E3,C12=3.37E3,C13=5.68E-4
PARAM C14=5.65E-9,C16=9.51E3,C18=9.51E3,C19=7.98E-4,C20=3.0E-9,
              D=2.87
PARAM RAIN=3504.7,H=-.1,RA=1.0E4
PARAM SLIP=7540.0,SLIW=2.00E4,SOURC=51.15,C21=4.8E3
INCON Q4Z=4.074E7,Q5Z=4.584E7,Q6Z=5.785E8,Q7Z=2.919E8,
              Q8Z=5.825E8
INCON Q9Z=1.925E8,Q10Z=1.59E10,Q11Z=4.314E11,Q12Z=5.506E11,
              Q5AZ=1.33E6
      R5=3435.*SINE(0.0,1.23E-5,4.71239)
      X1=Q6/A6
      X2=Q4/A4+Z
      Q4=INTGR(Q4Z,J1+J3A+(RAIN+R5)-C5*(X2-X1)+SLIW)
      X3=Q5/Q4
      Q5=INTGR(Q5Z,J1*J2+J3D*J3A+J6*(RAIN+R5)...
      -C7*J9*Q5+C8*J10*Q10-C9*X3*(X2-X1))
      C=Q5A/Q4
      Y5=COMPR(C,R2)
      Q5A=INTGR(Q5AZ,SOURC-C21*(Q5A/Q4)*(X2-X1)+SLIW
              *SLIP-C6*Q5A*Y5)
      X4=Q8/A8
      Q6=INTGR(Q6Z,J7+C5*(X2-X1)-C11*(X1-X4))
      Q7=INTGR(Q7Z,J7*J8+C9*Q5/Q4*(X2-X1)...
      -C12*Q7/Q6*(X1-X4)+C21*(Q5A/Q4)*(X2-X1)...
      -C13*J11*Q7+C14*J12*Q11)
      X5=H+D
      Q8=INTGR(Q8Z,C11*(X1-X4) C16*(X4-X5))
      Q9=INTGR(Q9Z,C12*Q7/Q6*(X1=X4)...
      -C18*Q9/Q8*(X4-X5)...
      -C19*J13*Q9+C20*J14*Q12)
      Q10=INTGR(Q10Z,C7*J9*Q5-C8*J10*Q10+C6*Q5A*Y5)
      Q11=INTGR(Q11Z,C13*J11*Q7-C14*J12*Q11)
      Q12=INTGR(Q12Z,C19*Q9*J13-C20*J14*Q12)
      A=Q7/Q6
      B=Q9/Q8
```

NOTE: DLS Computer Language described in: IBM System/1800 Digital Simulation Language Modeling Program, User's Manual.

Data for Simulation of the Nitrogen and Phosphorus Interaction Model (Fig. 25)

Parameter	Value of Parameter in the System	Pot Number	Pot Setting
J_3	3.0×10^{6}	11	.03
K_3	.126	12	.126
K_4	2.66×10^{-19}	13	.266
J_6	$.133 \times 10^{6}$	14	.001
J_4	7.5×10^{6}	15	.075
K_1	.126	16	.126
Q_5	42.6×10^{6}	21	.426
Q_4	3.38×10^{10}	22	.338
J_2	10.0	23	.055
K_9	21.0×10^{-19}	24	.210
K_8	$.94 \times 10^{-17}$	25	.094
K_2	3.7×10^{-20}	26	.370
K_7	.6	31	.600
I	6.7×10^{10}	32	.67
K_{13}	1.0	33	.999
Q_2	50.0×10^{6}	34	.5
Q_1	7.6×10^{6}	35	.076
K_6	.86	36	.860

SCALED EQUATIONS

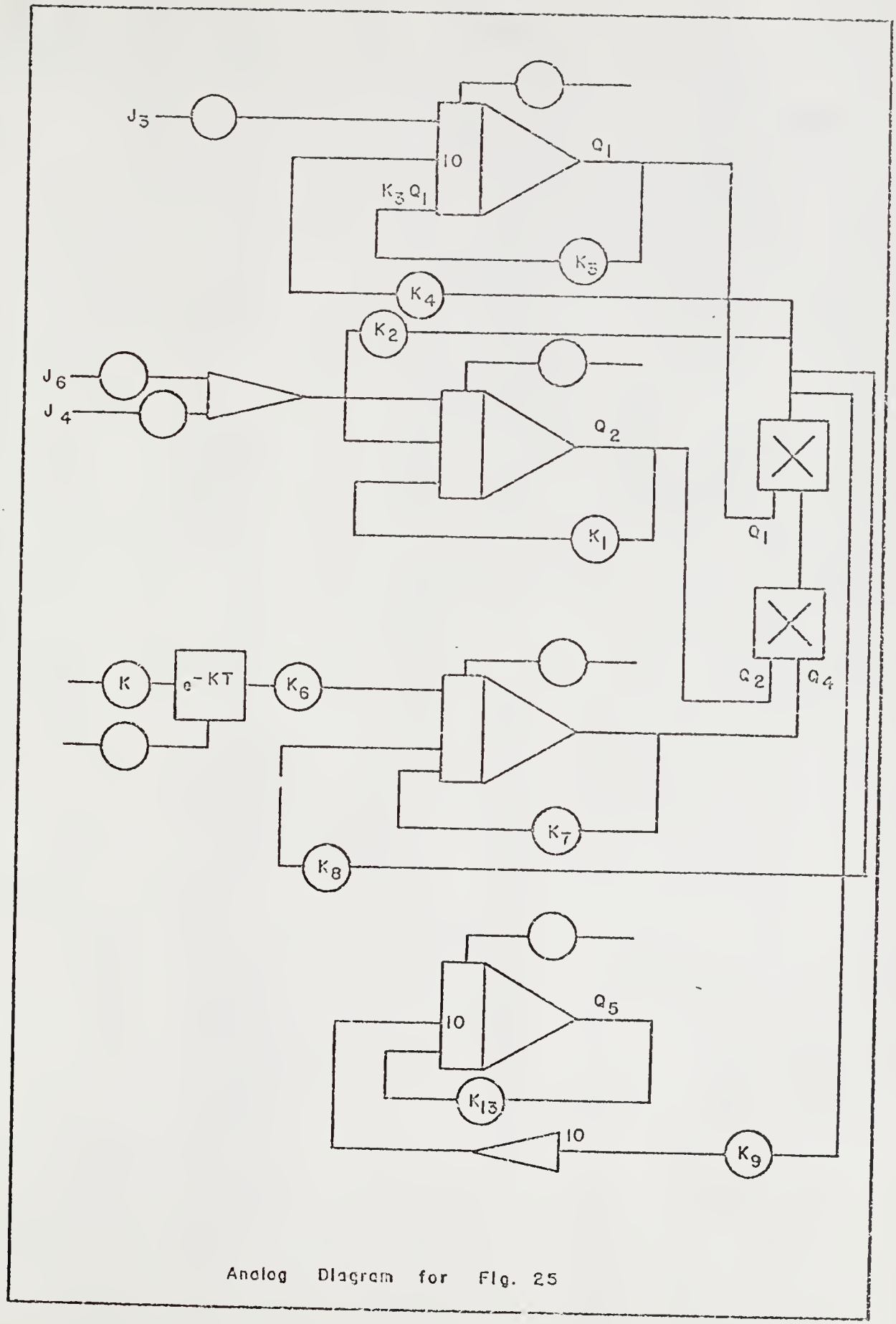
(FIG. 25)

$$\frac{\dot{Q}_1}{10^8} = .1\,\frac{J_3}{10^7} - .126\,\frac{Q_1}{10^8} - 2.66\left(\frac{Q_1}{10^8}\,\frac{Q_2}{10^8}\,\frac{Q_4}{10^{11}}\right)$$

$$\frac{\dot{Q}_2}{10^8} = .1\,\frac{J_6}{10^7} + 1.0\,\frac{J_4}{10^8} - .126\,\frac{Q_2}{10^8} - .37\left(\frac{Q_1}{10^8}\,\frac{Q_2}{10^8}\,\frac{Q_4}{10^{11}}\right)$$

$$\frac{\dot{Q}_4}{10^{11}} = .86\,\frac{1}{10^{11}}e^0 - .6\,\frac{Q_4}{10^{11}} - .094\left(\frac{Q_1}{10^8}\,\frac{Q_2}{10^8}\,\frac{Q_4}{10^{11}}\right)$$

$$\frac{\dot{Q}_5}{10^8} = 21.\left(\frac{Q_1}{10^8}\,\frac{Q_2}{10^8}\,\frac{Q_4}{10^{11}}\right) - .999\,\frac{Q_5}{10^8}$$



Analog Diagram for Fig. 25

Data for Simulation of the Simplified Geochemical Phosphorus Deposition Model (Fig. 38)

Parameter	Value of Parameter in the System	Pot Number	Pot Setting
Q_1	35.6×10^7	11	.356
Q_3	655.7×10^6	12	.655
J_3	350.0×10^5	13	.350
K_1	.218	14	.218
K_3	.156	15	.156
K_{10}	.08	16	.800
Q_2	$.29 \times 10^7$	21	.029
Q_4	$.625 \times 10^6$	22	.062
K_2	.0103	23	.103
K_7	.1024	24	.102
K_5	.05	25	.05
K_{11}	.208	26	.208
K_6	.363	31	.363
J_5	777.3×10^5	32	.777
J_4	1.5×10^5	33	.015
J_2	1.64×10^5	34	.164

SCALED EQUATIONS

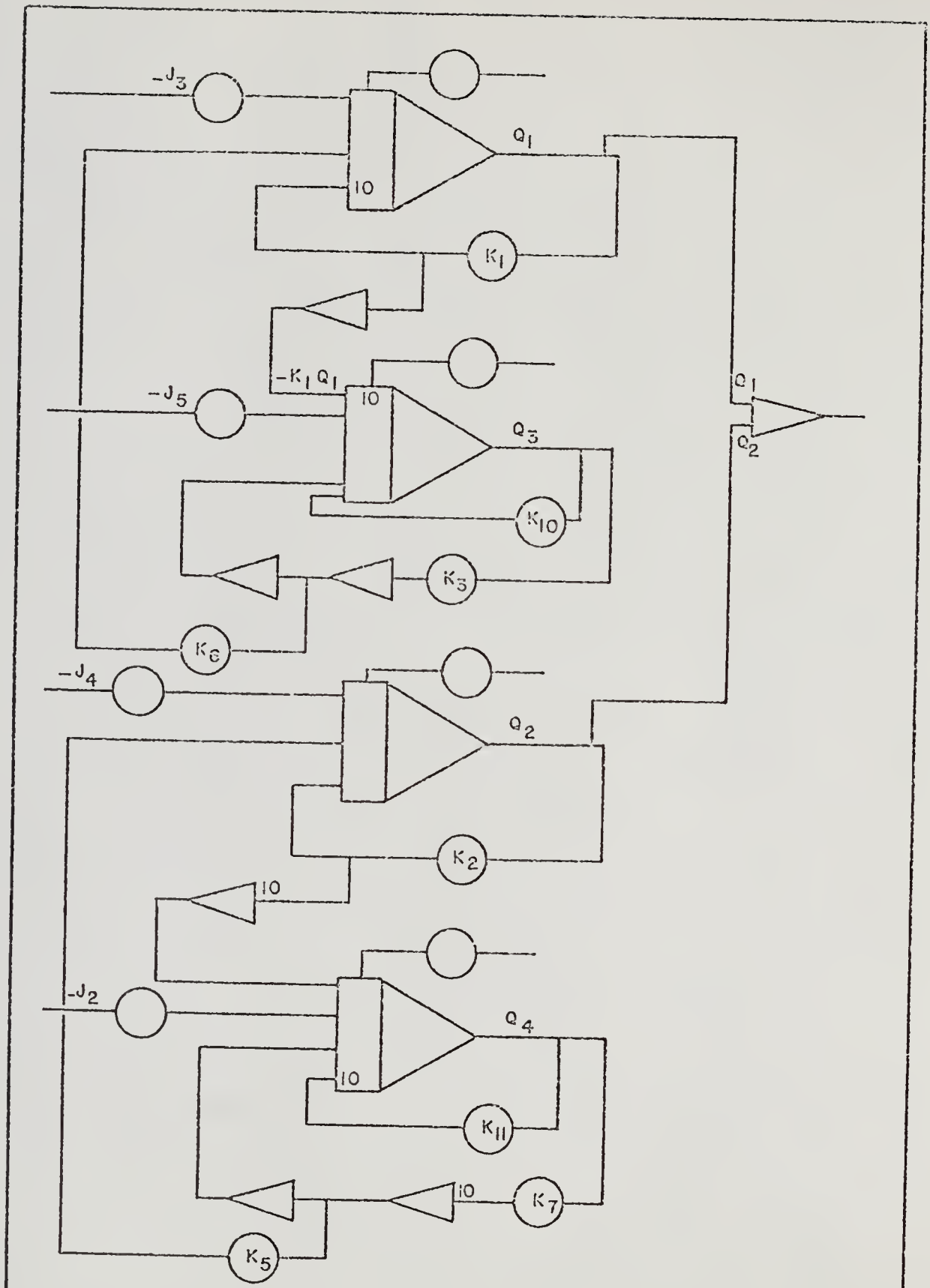
(FIG. 38)

$$\frac{\dot{Q}_1}{10^3} = .1\,\frac{J_3}{10^7} + .363\,\frac{Q_3}{10^9} - 2.18\,\frac{Q_1}{10^9}$$

$$\frac{\dot{Q}_2}{10^7} = 1.0\,\frac{J_4}{10^7} + .05\,\frac{Q_4}{10^6} - .103\,\frac{Q_2}{10^8}$$

$$\frac{\dot{Q}_3}{10^8} = 1.0\,\frac{J_5}{10^6} + 2.18\,\frac{Q_1}{10^9} - .156\,\frac{Q_3}{10^9} - .8\,\frac{Q_3}{10^9}$$

$$\frac{\dot{Q}_4}{10^6} = 1.0\,\frac{J_2}{10^6} + 1.03\,\frac{Q_2}{10^8} - 1.02\,\frac{Q_4}{10^7} - 2.08\,\frac{Q_4}{10^7}$$

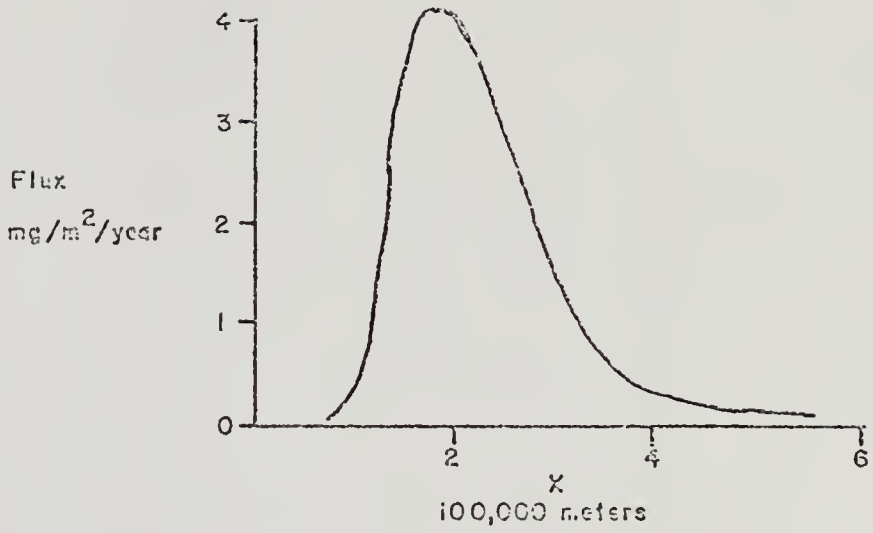


ANALOG DIAGRAM for Fig. 38

APPENDIX C

DATA FOR SOLUTION OF BROOKS EQUATION

RESULTS:



Brooks (1960) Equation: $\frac{\partial}{\partial y}\left(-Ey\frac{\partial c}{\partial y}\right) + U\frac{\partial c}{\partial x} = 0$

U = velocity in X direction (along loop current of fig. 1) = $1\ \frac{m}{s}$

Ey = eddy diffusivity in the y direction toward Florida = $10^3\ m^2/sec$

C = concentration = $.03 g/m^3$

y = 100 miles

x = taken at 25mile intervals from 50 to 350 miles

General Solution with no decay of phosphorus (Brooks 1960):

$$c(x,y) = \frac{Co}{2\sqrt{\pi Eyt'}} \int_{-\frac{b}{2}}^{\frac{b}{2}} \exp\left(-\frac{(y_1 - y')^2}{4Eyt'}\right) dy'$$

where for the 4/3 law for Ey

$$t' = \frac{x'}{U}$$

$$x' = \frac{b}{2\beta}\left[\left(1 + \frac{2}{3}\beta\frac{x}{b}\right)^3 - 1\right]$$

$$\mathcal{S} = \frac{12\,Ey}{Ub}$$

b = width of source = 10 miles

The derivative yields a flux:

$$\frac{dc}{dy} = \frac{12\,Co}{\sqrt{\pi}\,b^2\left[\left(1+\frac{2}{3}\mathcal{S}\frac{x}{b}\right)^3-1\right]}\left\{-\exp-\frac{\frac{3}{2}\quad\frac{4}{b^2}}{\left[\left(1+\frac{2}{3}\mathcal{S}\frac{x}{b}\right)^3-1\right]}\left(y_1+\frac{b}{2}\right)^2+\right.$$

$$\left.\exp-\left(\frac{\frac{3}{2}\quad\frac{4}{b^2}}{\left(1+\frac{2}{3}\mathcal{S}\frac{x}{b}\right)^3-1}\quad\left(y_1-\frac{b}{2}\right)^2\right)\right\}$$

Final Flux $= Ey\frac{dc}{dy}$ in $g/m^2/sec.$

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BIOGRAPHICAL SKETCH

Martha Winters Gilliland was born November 22, 1944, at Lancaster, Pennsylvania. In June, 1962, she was graduated from Manheim Township High School. In June, 1966, she received the degree of Bachelor of Arts with honors from Catawba College, Salisbury, North Carolina. With a National Science Foundation Traineeship, she enrolled in the Graduate School of Rice University, Houston, Texas, in September, 1966. She received the degree of Master of Arts in June, 1968, with a major in geology and geophysics. From 1968 to 1970, she was employed as instructor of physical sciences at Santa Fe Community College, Gainesville, Florida. From September, 1970, until the present time she has been enrolled in the Graduate School of the University of Florida. She received an Environmental Protection Agency research fellowship in January, 1972, under which work toward the degree of Doctor of Philosophy was pursued.

Martha Winters Gilliland is married to John Richard Gilliland and is the mother of two children.

I certify that I have read this study and that in my opinion it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation for the degree of Doctor of Philosophy.

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August, 1973

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